A PRACTICAL GUIDE TO IRON AND STEEL WORKS ANALYSES

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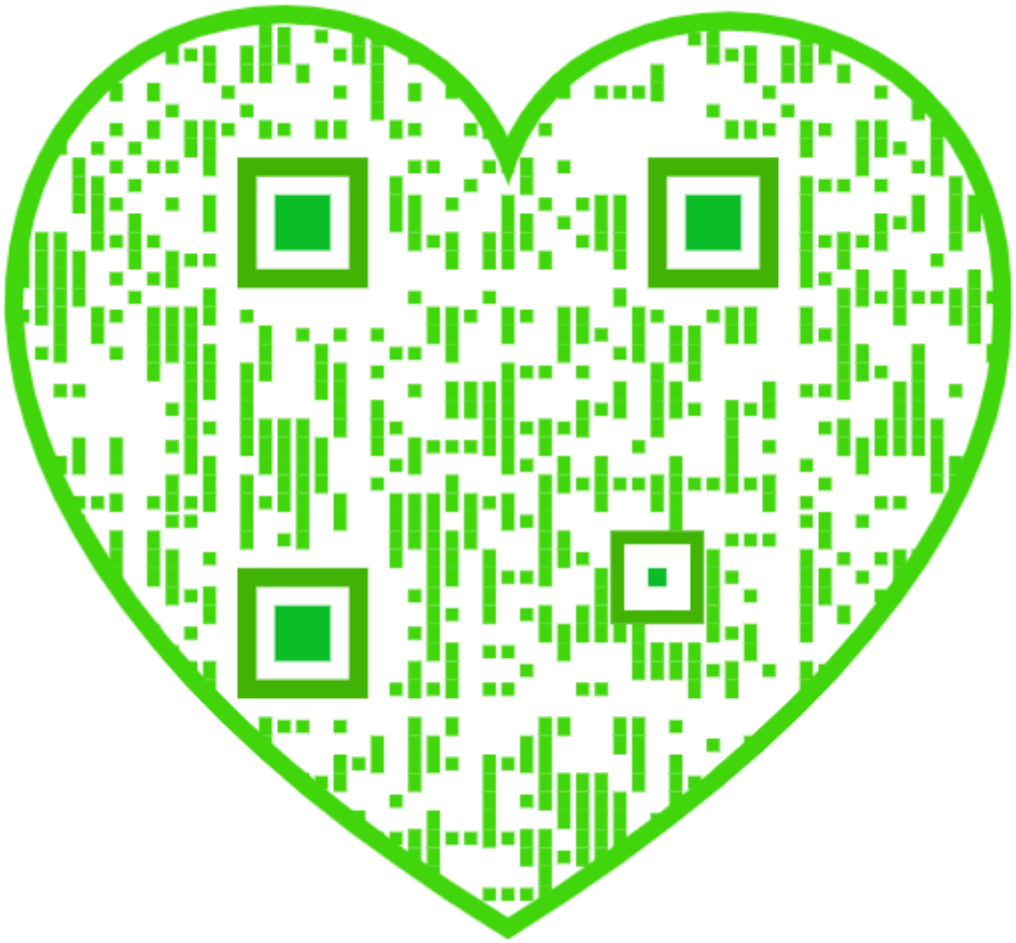
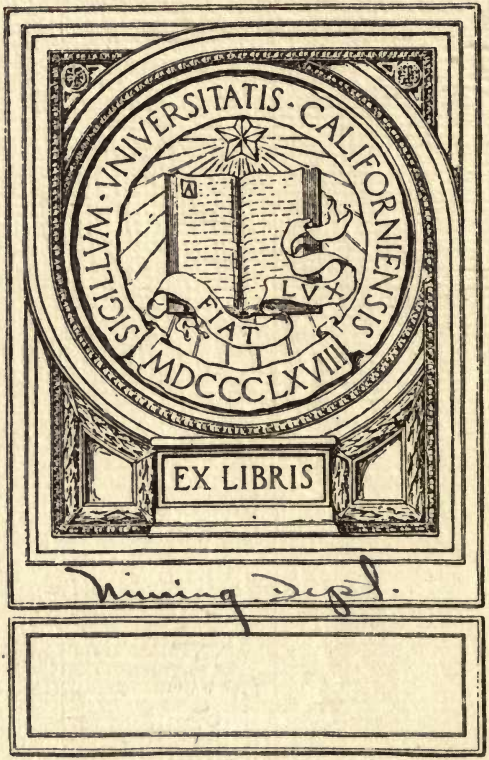
WALTER MACFARLANE, F.I.C.

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A PRACTICAL GUIDE TO

IRON AND STEEL WORKS ANALYSES

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A PRACTICAL GUIDE TO IRON AND STEEL WORKS ANALYSES

BEING

SELECTIONS FROM "LABORATORY NOTES ON IRON AND STEEL ANALYSES"

BY

WALTER MACFARLANE, F.I.C.

PRINCIPAL OF THE METALLURGICAL DEPARTMENT, STAFFORDSHIRE EDUCATION COMMITTEE
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AND VICE-PRESIDENT WEST OF SCOTLAND IRON AND STEEL INSTITUTE

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PREFACE.

THIS Guide has been compiled from the successful volume, *Laboratory Notes on Iron and Steel Analyses*, to meet the requirements of those who do not wish to enter for the complete analytical course.

Notes on Fuel Analyses have been added.

THE MUNICIPAL SCIENCE SCHOOL,
WEDNESBURY, *December*, 1910.

EXTRACT FROM THE PREFACE

TO

LABORATORY NOTES ON IRON AND STEEL ANALYSES.

THESE notes were in the first instance written for the guidance of the staff in an iron and steel works laboratory, which was for some years under the supervision of the author, and where the results of over 40,000 estimations were annually placed on record.

The methods required to be reliable and rapid so as to control and keep pace with the manufacturing operations. It was necessary that all the analysts should work on identical lines. By estimations made at intervals on standard substances, uniform results were regularly obtained from all the members of the staff in the laboratory. The accuracy of the methods was tested in daily practice, and confirmed by analysts acting on behalf of buyers and sellers at home and on the Continent.

The general aim of the book has been to set out the complete course of an assay or an analysis in full detail. In many cases whole paragraphs have

been reintroduced, where necessary, to obviate the confusion arising from cross references.

The analytical methods are given in detail, precise quantities are stated, and the most convenient sizes of beakers, &c., are specified. In these there is no intention of imperiousness. Time and money can be saved by avoiding the waste due to the use of unnecessary excess of chemicals. Good results have been obtained in every-day practice by implicitly following the instructions embodied in the notes. But they must be followed thoughtfully : no book of directions can be a substitute for brains.

Examples of calculations are freely given throughout the notes, as these have been found to be helpful.

The preparation of the necessary solutions is dealt with in a separate part of the book. This arrangement has many advantages.

July, 1909.

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ATOMIC WEIGHTS

USED IN THIS BOOK.

	Chemical Symbol.	Atomic Weight.		Chemical Symbol.	Atomic Weight.
Aluminium,	Al	27·1	Molybdenum,	Mo	96·0
Arsenic, . .	As	75·0	Nickel, . .	Ni	58·7
Barium, . .	Ba	137·4	Nitrogen, .	N	14·04
Cadmium, .	Cd	112·4	Oxygen, . .	O	16·0
Calcium, .	Ca	40·1	Phosphorus,	P	31·0
Carbon, . .	C	12·0	Potassium, .	K	39·15
Chlorine, .	Cl	35·5	Silicon, . .	Si	28·4
Chromium, .	Cr	52·1	Silver, . .	Ag	107·9
Cobalt, . .	Co	59·0	Sodium, . .	Na	23·0
Copper, . .	Cu	63·6	Sulphur, .	S	32·06
Fluorine, .	F	19·0	Tantalum, .	Ta	181·0
Hydrogen .	H	1·0	Titanium, .	Ti	48·10
Iodine, . .	I	127·0	Tungsten or		
Iron, . . .	Fe	55·9	Wolfram,	W	184·0
Magnesium,	Mg	24·36	Vanadium, .	V	51·2
Manganese,	Mn	55·0			

ATOMIC WEIGHTS, REVISED 1909.

Iodine, . . .	126·92	Silicon, . . .	28·3
Manganese, . .	54·92	Sulphur, . . .	32·07

LABORATORY NOTES

ON

IRON AND STEEL ANALYSES.

ANALYSIS OF STEEL.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample to be tested is treated exactly in the same manner, and the solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

Notes on the Process.

The standard steel ought to have a composition approximating to that of the sample.

Siemens steel should be tested against Siemens steel, basic Bessemer steel against basic Bessemer steel, &c.

The standard and the sample steels should preferably have undergone the same thermal and mechanical treatment.

The mechanical condition of the standard and the sample should not differ widely.

A steel containing a high percentage of carbon requires more acid than one which contains a low percentage of carbon. A high-carbon steel requires to be heated during solution longer than a low-carbon one. But, obviously, both standard and sample ought to be treated with an equal amount of acid, and be heated for the same length of time.

The graduated Eggertz' tubes should be capable of containing 20 c.c. They should be of clear glass, and the bore of each should be equal to others of the same set. Each Eggertz' tube should have a ground glass stopper, or be bent at the top (see p. 158).

The amount of cold solution should be between 3 and 8 c.c. This reservation is now ignored.

The amount of carbon found by the colour test

may differ from that found in the same piece of steel after reheating, annealing, or other treatment.

Certain metals, such as chromium, copper, and nickel, interfere with the accuracy of the colour test for carbon.

In works' practice, the percentage of carbon in a steel is, as a rule, approximately known before being handed in to the laboratory. A suitable standard can therefore be chosen. If, however, the percentage of carbon in the standard differs too much from that of the steel which is being tested, another standard steel should be taken and a fresh comparison made.

The quantity of steel and acid taken for a test should, in some degree, correspond to the percentage of carbon present.

Suitable quantities are :—

For very soft steel, such as is produced for electrical purposes, with carbon under 0·05 per cent., it is advisable to work on 0·3 gramme of the sample dissolved in 5 c.c. of 1·2 specific gravity nitric acid.

For ordinary mild steel, as supplied for structural purposes, with about 0·18 per cent. of carbon, 0·2 gramme may be weighed off and treated with 3·5 c.c. of 1·2 specific gravity nitric acid.

For medium steel—for rails, tyres, axles, &c., containing from about 0·3 to 0·6 per cent. of carbon—0·1 gramme of steel and 2 c.c. of 1·2 specific gravity nitric acid may conveniently be used.

For tool steels, with carbons ranging from 0·75 to

1·5 per cent., 0·10 gramme of the steel dissolved in 5 c.c. of 1·2 specific gravity nitric acid are convenient quantities.

In every case the weighed-off standard and sample should be treated with a like quantity of acid, and under exactly similar conditions.

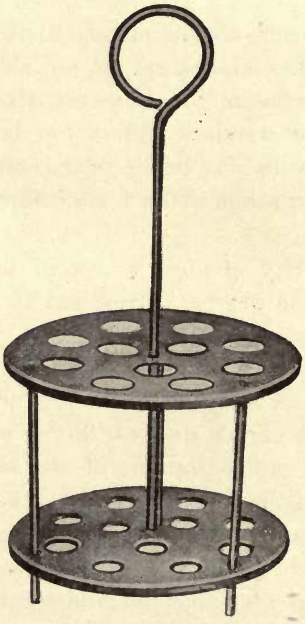

Fig. 1.—Rack for test tubes.

Details of the Process.—Weigh off a convenient quantity of a suitable standard steel, prepared as directed on pp. 11 and 12.

Transfer the weighed quantity to a 13 × 1·3 cm.

(about 5-inch × ½-inch) clean, dry test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

The test tube may be conveniently placed in the kind of rack shown in Fig. 1.

Weigh off a similar quantity of each sample of steel which is to be tested.

All drillings and turnings must be clean, and free from scale, oil, &c.

Transfer each weighed portion to a separate test tube, and note the sample number on each label.

To each weighed quantity measure the required volume of 1·2 specific gravity nitric acid.

When brisk action has ceased, set the test tube rack, with contents, in a bath of boiling water, and keep the bath at boiling point until all the steels are dissolved.

Take the test tube rack and contents from the hot bath, and set to cool in a dish of cold water.

When the solutions have cooled, proceed to compare the relative depths of colour.

The stand shown in Figs. 2 and 3 is useful. It provides a rack for the Eggertz' tubes, supports for the burette from which the acid is measured, support for the burette from which the water for dilution can be conveniently added, and a frame for carrying a light diffuser. A thin pane of ground glass may be fitted, or a piece of filter paper may be gummed on to the frame, or a pane of clear glass may be fitted, to which a piece of wet filter paper may be fastened—it will

easily be made to adhere—before making colour comparisons. A small cutting of rubber tubing is placed at the bottom of each tube recess to act as a pad. Over each burette an inverted test tube is placed to keep out dust.

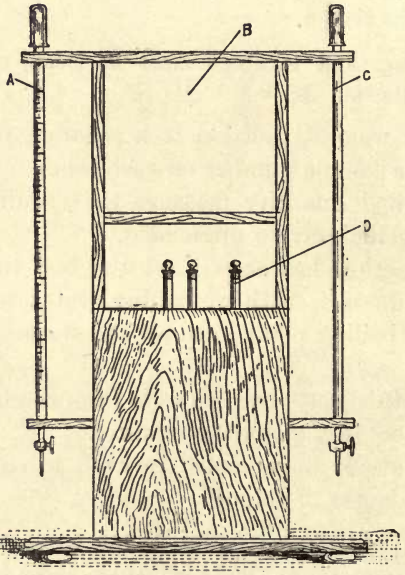

Fig. 2.—Stand for Eggertz' tubes—Front view.

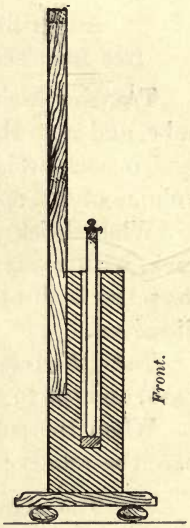

Fig. 3.—Stand for Eggertz' tubes—Cross section.

A, Burette for measuring acid.
B, Frame for light diffuser.
C, Burette for water. D, Eggertz' tube.

To compare the coloured solutions, pour from the standard test tube into a graduated Eggertz' tube which has a distinguishing mark, such as a rubber

ring or a mark made with a diamond. With a fine jet of cold water rinse the test tube, and drain the rinsings into the graduated tube.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Transfer the solution from the other test tube to a corresponding Eggertz' tube. Rinse, drain, and mix as before.

Compare the depth of colour of the two solutions.

> NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker coloured solution with cold water, mix well and compare again.

If necessary, dilute further, mix and compare. Repeat until the solution from the sample is of the same depth of tint as that of the standard.

Read off the volumes of the solutions, and calculate the result.

GENERAL RULE FOR CALCULATING.—Divide the percentage carbon of the standard steel by the volume of its solution, and multiply the result by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0·21 per cent. of carbon, and the solution was diluted to 6·3 c.c. The solution from the sample required to be diluted to 5·4 c.c.

Then $$\frac{0{\cdot}21}{6{\cdot}3} \times 5{\cdot}4 = 0{\cdot}18.$$

0·18 = percentage of carbon in the sample, as shown by the colour test.

It is usual to dilute the solution from the standard steel to such a volume that the percentage of carbon in the sample can be directly read off, or so that only a simple calculation is necessary.

EXAMPLE.—Standard steel contained 0·51 per cent of carbon, and the solution was diluted to 5·1 c.c.

The solution from the sample required to be diluted to 5·7 c.c.

∴ Percentage of carbon in the sample, as shown by the colour test = 0·57 per cent.

In the first example the solution from the standard steel was purposely diluted so that every 0·1 per cent. of carbon had 3 c.c. of liquid = 30 measures for each 1 per cent.—

$$\frac{6{\cdot}3}{30} = 0{\cdot}21.$$

Similarly, we divide the number of c.c. to which the solution from the sample was diluted—

$$\frac{5{\cdot}4}{30} = 0{\cdot}18.$$

0·18 = percentage of carbon in the sample.

Rapid Estimation of Carbon in Furnace Samples.

A sample of the "metal" is taken from the furnace in a "spoon," allowed to solidify, hammered, cooled, and drilled. The drillings are quickly tested by:—

Weighing off a suitable quantity of the drillings, dissolving in dilute nitric acid, using a small Bunsen burner to hasten the action of the acid, cooling under a water tap, transferring to an Eggertz' tube and comparing with a suitable standard. For very soft steels, it is not unusual to take 0·5 gramme of the drillings, and, having dissolved and cooled, diluting to about 20 c.c., and comparing in long Eggertz' tubes.

Estimation of Minute Quantities of Carbon.

J. E. Stead described* a new method for the estimation of minute quantities of carbon. This consists in adding solution of potash or soda to the nitric acid solution. The depth of colour is about two and a half times that of the acid solution.

The estimation is carried out thus: 1 gramme of the steel or iron to be tested is weighed off and placed in a 200 c.c. beaker, and, after covering with a watch-glass, 12 c.c. of nitric acid of 1·2 specific gravity are added. The beaker and contents are then placed on a warm plate, heated to about 90° to 100° C., and there allowed to remain until dissolved, which does not usually take more than ten minutes. At the

* *Journal of The Iron and Steel Institute*, No. 1, 1883, p. 213.

same time, a standard steel containing a known quantity of carbon is treated in exactly the same way, and when both are dissolved, 30 c.c. of hot water is added to each and 13 c.c. of standard solution of sodium hydrate of 1·27 specific gravity.

The contents are now to be well shaken, and then poured into a glass measuring-jar and diluted till they occupy a bulk of 60 c.c. After again well mixing and allowing to stand for ten minutes in a warm place, they are filtered through dry filters, and the filtrates, only a portion of which is used, are compared. This may be done by pouring the two liquids into two separate measuring tubes in such quantity or proportion that upon looking down the tubes the colours appear to be equal.

Thus if 50 mm. of the standard solution is poured into one tube, and if the steel to be tested contains, say, half as much as the standard, there will be 100 mm. of its colour solution required to give the same tint. The carbon is, therefore, inversely proportional to the bulk compared with the standard, and in the above assumed case if the standard steel contained 0·05 per cent. carbon, the following simple equation would give the carbon in the sample tested:—

$$\frac{0{\cdot}05 \times 50}{100} = 0{\cdot}025.$$

In the same interesting paper Stead describes a simple but efficient instrument for colour estimations. See pp. 158 and 159.

Preparation of Standard Steel for Colour Test.

Procure a billet of steel of average composition and containing a suitable percentage of carbon. The steel selected must not have been overheated or subjected to any treatment having a tendency to alter the condition of the carbon—at least not more than superficially. On one side of the billet drill, with a broad drill, a series of holes of depth enough to permit the drill to more than clear a quarter of an inch below the surface.* Reject these drillings.

With a smaller drill continue for a short distance in. to drill a little from each of the holes. Collect these drillings. Drill a little more out of each hole and collect the drillings. If drilling is continued too long in any hole, the drillings become pulverised and worthless. The pulverising action increases with the depth of the hole, so that it is advisable to begin operations on another side of the billet rather than drill too deeply.

Care must be taken to keep oil and dust from the drillings.

When enough drillings have been collected, the finer portions and the rougher portions are separated by sifting, and are rejected. The remainder should

* If more convenient the billet may be planed or turned rather than drilled, but all surface planings or turnings must be rejected.

be very well mixed and put away in a clean, dry, well-stoppered bottle; the stopper and neck being covered with india-rubber or parchment, and kept in a dry place. From that stock small quantities may be taken from time to time for daily use.

The percentage of carbon in the standard may be accurately ascertained by combustion, and should be compared with standards in use in good steel works and public laboratories.

ESTIMATION OF SILICON IN STEEL.

Outline of the Process.—When mild steel containing silicon is dissolved in hydrochloric acid, and the solution is evaporated to thorough dryness, the silicon becomes oxidised. On boiling the dried residue in hydrochloric acid, all the other components of ordinary mild steel are dissolved. The insoluble residue is collected on a filter, washed, dried, ignited, and weighed, and the percentage calculated.

If there is reason to suspect that the weighed residue is not pure silica (SiO_2), it may be fused with potassium bisulphate, washed, ignited, &c.

Details of the Process.—Weigh off 4·702 grammes of the sample.

Transfer the weighed portion to a 13 × 11·5 cm. (about 5-inch × 4½-inch) Jena or Bohemian * beaker.

Add 40 c.c. of hydrochloric acid of 1·16 specific gravity. This is of the specific gravity usually sold.

Evaporate on a hot plate to dryness. The residue should be well dried, but not "burnt" (see note on "hot plate," p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

* The size of beaker specified here and in other pages is not imperative. But it is more satisfactory to state a convenient size than to print "a medium-sized beaker."

with liquid, add 50 c.c. of hot water and 35 c.c. of hydrochloric acid of 1·16 specific gravity.

Boil for a few minutes to dissolve the ferric chloride, &c. Add about 80 c.c. of hot water.

Filter, using a 9 cm. Swedish filter.

Carefully remove the last granules of silica from the inside of the beaker on to the filter, using a "bobby" (a glass rod with a rubber tip) if necessary.

Wash the residue on the filter three or four times with dilute hydrochloric acid—1 of specific gravity 1·16 acid to 6 of water.

Wash several times with hot water.

All traces of colour should be removed from the filter paper and the precipitate. If washing does not effect this, the residue must be purified by fusion (see next page for details).

Fig 4.—Filter dryer.

If the residue is white, or of a grey tint on account of a little finely-divided graphite, dry it by placing the funnel with filter paper and contents on a filter dryer (Fig. 4), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter paper in a tared platinum or porcelain crucible or capsule.

In a hot muffle furnace (Fig. 5) burn off the filter paper, and ignite for about half an hour.

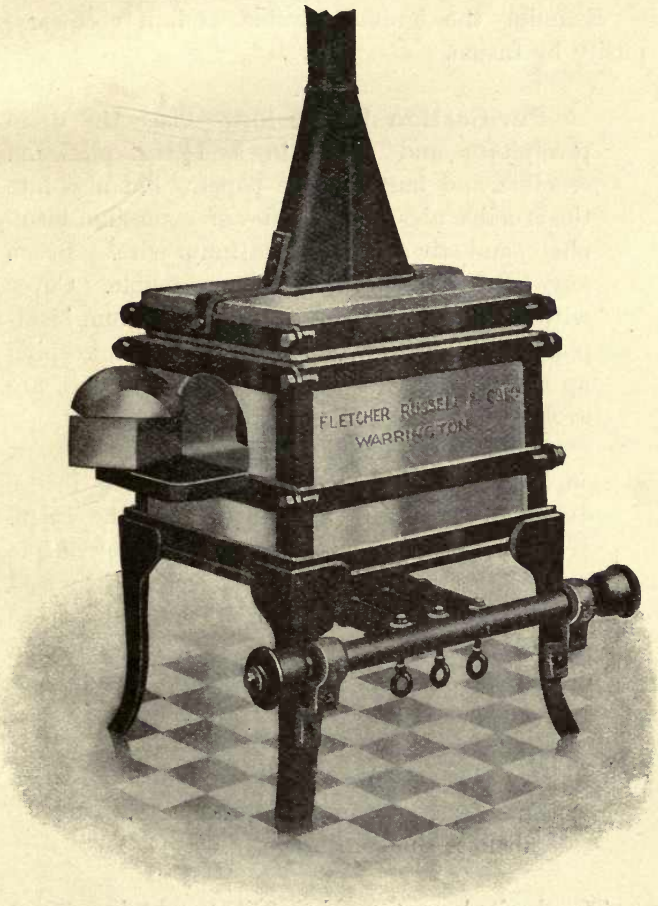

Fig. 5.—Muffle furnace.

Withdraw the crucible, &c., and allow to cool in a desiccator.

Weigh quickly, and note the weight.

Examine the ignited residue, and, if necessary, purify by fusion.

Purification by Fusion.—Place the dried precipitate and paper in a 1½-oz. platinum crucible, and burn off the paper. Put also into the crucible about 3 grammes of potassium bisulphate, and stir up with a platinum wire. Brush any adhering matter into the crucible. Cover with about 1½ grammes more of potassium bisulphate, and fuse the whole, gently at first, keeping up the temperature as long as white fumes are evolved.

When the crucible has cooled a little, set it on its side in a deep porcelain basin, 5 inches diameter, and pour hot water into the basin. When the melt has loosened, take out the crucible and wash the contents into the basin. Stir well so as to dissolve as much of the sulphate as possible. Filter through a 12·5 cm. Swedish filter paper. Wash until all traces of sulphate are removed. Sometimes about 1 litre of water is required.

Dry the washed precipitate, ignite, allow to cool in a desiccator, and weigh quickly.

Calculate the percentage.

The ignited pure residue (SiO_2) contains 47·02 per cent. of silicon, and when 4·702 grammes of

sample are operated on, the factor for calculation is

$$\frac{47{\cdot}02}{4{\cdot}702} = 10.$$

EXAMPLE— Grammes.

Weight of silica + ash + crucible	=	17·1354
„ crucible . . .	=	17·1312
„ silica + ash . .	=	0·0042
„ ash	=	0·0007
„ silica . . .	=	0·0035

0·0035 × 10 = 0·035 = percentage of silicon in the sample.

If a quantity other than 4·702 grammes be taken for analysis, calculate thus—

$$\frac{\text{Weight of silica} \times 47{\cdot}02}{\text{Weight of sample taken}} = \text{percentage of silicon.}$$

Log 47·02 = 1·6722826.

ESTIMATION OF PHOSPHORUS IN STEEL.

The Molybdate Method.

Outline of the Process.—The phosphorus in the weighed portion of the sample is oxidised to phosphoric acid, which can, in a properly regulated solution, form a precipitate, $[(NH_4)_3PO_4 . 12MoO_3]$, containing a definite percentage of phosphorus. The precipitate is collected, washed, dried, and weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation. If the weight of the precipitate exceeds 0·3 gramme its composition may be irregular.

Details of the Process.—For mild and medium steels which are free, or practically free, from arsenic.

Weigh off 2 grammes of the drillings.

Transfer the weighed portion to a 14 × 13 cm. (about 5½ × 5-inch) spouted Jena or Bohemian beaker. A wide beaker facilitates evaporation ; a tall beaker minimises risk of loss by spirting.

Add 20 c.c. of 1·42 specific gravity nitric acid along with 7 c.c. of water. Higher carbon steels require more acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149). When, towards the end of the evaporation, there is much danger of loss by spirting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for five minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 15 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much as possible. The solution and washings should not measure more than 15 c.c.

Add 17 c.c. of ammonium nitrate solution (see p. 163).

Heat to about 90° C.

Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 15 c.c. of molybdate solution (see p. 162) into the flask. This

will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Rinse any remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1·42 specific gravity) to 50 of water.

Open out the filter paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate into a tared porcelain basin or a basin of platinised nickel—see note on p. 150.

Evaporate on the water bath (Fig. 6) till the precipitate is completely dried.

This water bath consists of an oblong copper box with inlet. On the top are two openings cut to suit the size of the evaporating basins. Copper covers are provided for these openings. These have openings to suit the test tubes required for dissolving a few samples of steel for carbon estimations. The water supply is stored in a Winchester quart or other glass bottle which is fitted with a two-hole rubber stopper. Glass tubing is arranged as shown in the illustration. To start the bath, the bottle is nearly filled with water, the stopper, with the tubes, is placed in position and set on the wooden stand. On

blowing into the curved glass tube, water is forced through the syphon tube into the water bath, into which it will continue to flow till it rises to the level of the bottom of the curved

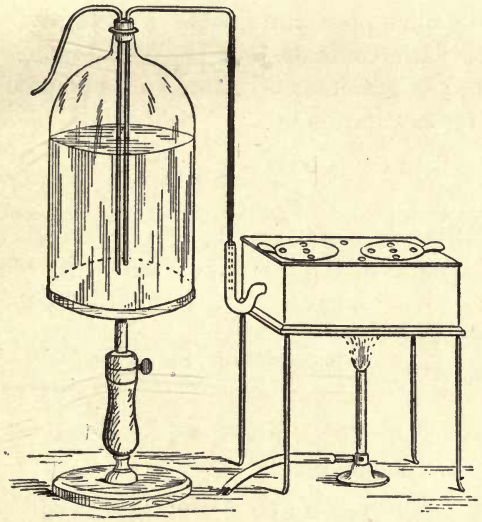

Fig. 6.—Water bath, with constant level water supply.

tube. The water level in the bath will remain practically constant until the supply is exhausted. The bath is mounted on an iron stand, and heat is applied from a Bunsen burner.

Wipe the outside of the basin and allow it to cool. Weigh, and calculate the result.

Other plans are (*a*) to use counterpoised filter-papers, (*b*) to brush the dried precipitate

on to a tared watch-glass, and (*c*) to estimate by standardised solutions. The author prefers to wash the precipitate into the tared basin and dry it on the water bath.

The yellow precipitate, when thoroughly dried on a water bath, contains 1·63 per cent. of phosphorus, and when 2 grammes of sample are operated on the factor for calculation is

$$\frac{1{\cdot}63}{2} = 0{\cdot}815.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate	= 23·184
„ basin . . .	= 23·125
„ precipitate . .	= 0·059

0·059 × 0·815 = 0·048 = percentage of phosphorus in the sample.

$$\text{Log } 0{\cdot}815 = \bar{1}{\cdot}9111576.$$

When phosphorus in steel is estimated in strict accordance with the foregoing details, the result may be accepted as reliable.

The following modification has advantages, but requires practice to ensure concordant results:—

Weigh off 2 grammes of the drillings.

Transfer the weighed portion to a 10·2 × 7 cm. (4-inch × 2¾-inch) beaker.

Add 40 c.c. of 1·20 specific gravity nitric acid.

Heat till the drillings are dissolved.

Add 10 c.c. of a 1 per cent. solution of potassium permanganate.

Boil till the brown precipitate has dissolved and the pink colour has disappeared.

Cautiously add sulphurous acid (see p. 172) till the solution becomes clear.

Boil off the slight excess of acid and allow to cool.

Add 20 c.c. of 0·88 specific gravity ammonia solution.

Add strong nitric acid till the liquid in the beaker turns to a light sherry colour.

Add not less than 25 c.c. of molybdate solution—prepared by dissolving 100 grammes of ammonium molybdate in 1 litre of water—and, immediately after, add 6 c.c. of strong nitric acid.

The precipitate soon settles, and is filtered, washed, and weighed as in the method described on p. 20.

Estimation by Titration.

Instead of weighing the yellow phospho-molybdate precipitate, it is convenient, when a large number of determinations are to be made, to estimate the phosphorus volumetrically. For this purpose wash the precipitate six times with the usual 2 per cent. nitric acid solution, and afterwards with a 2 per cent. solution of sodium sulphate till free from acid. Open out the filter-paper, and, with a fine-jet wash-bottle containing hot water, wash the precipitate off the paper into a beaker. Measure, from a burette, standard sodium hydrate solution till the precipitate is dissolved, then run in a slight

excess, and note the amount used. Add two or three drops of phenol-phthalein solution to act as an indicator. Then measure, from a burette, standard sulphuric acid or nitric acid solution till change of colour is effected. The solution in the beaker should, of course, be constantly stirred during the addition of the standard acid.

The nitric acid solution may be standardised by pure sodium carbonate (Na_2CO_3), and the caustic soda solution then standardised by the nitric acid. Or, having ascertained the relative strengths of the acid and alkaline solutions, the latter may be standardised by titrating the solution from 2 grammes of steel of known percentage of phosphorus.

Walter Rosenhain states* that when the precipitate is washed with water alone the results agree closely with those obtained on washing with nitric acid and ammonium nitrate. His comparative figures show that water-washing gives a slightly higher result.

Rapid Estimation of Phosphorus in Furnace Samples.

For the very rapid approximate estimation of phosphorus in the "metal" in a basic furnace, two previously-prepared solutions are required, viz.:—

No. 1 solution, made by dissolving 200 grammes of ammonium nitrate in about 150 c.c. of hot water, allowing to cool, adding 250 c.c. of strong nitric acid (say 1·4 specific gravity), and making up to 500 c.c.

* *Iron and Steel Institute Journal*, vol. i., 1908.

No. 2 solution, made by dissolving 50 grammes of ammonium nitrate in about 200 c.c. of hot water, allowing to cool, adding 40 grammes of ammonium molybdate dissolved in 200 c.c. of water, and making up to 500 c.c.

A sample of the "metal" is taken from the furnace in a "sample spoon," allowed to solidify, hammered, cooled, drilled, and quickly tested thus:—

Weigh off 0·2 gramme of the drillings.

Transfer the weighed portion to a 15 cm. × 1·6 cm. (about 6 × $\frac{5}{8}$ inch) test tube.

Add 4 c.c. of No. 1 solution.

Heat till the drillings are dissolved.

Add 4 c.c. of No. 2 solution.

Warm the solutions.

Shake the tube to facilitate the precipitation.

Compare with the amount of the precipitate from a like quantity of a steel of known percentage of phosphorus which has been similarly treated in a corresponding test tube.

Molybdate and Magnesia Method.

For check analyses, especially in disputed cases, it is advisable to employ a good alternative method, and the one in which the product weighed at the end is pure magnesium pyrophosphate, is, with care and experience, reliable.

Outline of the Process.—A weighed quantity of the sample is dissolved in nitric acid, and evaporated to dryness and roasted. The dried mass, containing the phosphorus in its most highly oxidised

state, is dissolved in acid and neutralised. Nitric acid, ammonium nitrate, and molybdate solutions are added to cause the precipitation of a yellow compound [$(NH_4)_3PO_4.12MoO_3$] containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the other constituents of the steel. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 14 × 13 cm. (about 5½ × 5 inch) spouted Jena or Bohemian beaker.

Add 40 c.c. of 1·42 specific gravity nitric acid, along with 10 c.c. of water.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149). When, towards the end of the evaporation, there is much danger of loss by spirting, interpose a thin piece of wire gauze between the plate and the beaker. The evaporation will then proceed more quietly till finished.

Allow the beaker to remain on the hot plate for ten minutes more, so as to oxidise all the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact

with liquid, add 35 c.c. of 1·16 specific gravity hydrochloric acid, and allow to boil until the contents of the beaker have dissolved.

Continue the boiling till the bulk of the solution has been reduced to about one-half.

Neutralise the excess acid by cautiously adding ammonia liquor.

Add more ammonia liquor to form a slight permanent precipitate.

Dissolve the precipitate by adding 1·42 specific gravity nitric acid, and stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, about 33 c.c. of molybdate solution (see p. 402) into the beaker. This will cause the formation of a yellow precipitate containing the phosphorus.

Stir the solution vigorously to hasten precipitation.

Allow to settle at a temperature under 100° C. for about fifteen minutes.

Pour the solution with the yellow precipitate into a 9 cm. close-texture filter. Rinse any remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1·42 specific gravity nitric acid to 50 of water, collecting the filtrate and washings in a beaker.

Remove the beaker containing the filtrate and washings, and place a clean 350 c.c. (about 12-oz.) conical flask under the funnel.

Dissolve the precipitate by means of a dilute

solution of ammonia—say 1 of 0·880 specific gravity ammonia liquor to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0·880 specific gravity ammonia liquor

Add about 5 c.c. of magnesia mixture (see p. 167).

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate, $Mg(NH_4)PO_4.6H_2O$. Allow the precipitate to settle for about an hour.

Decant the clear solution through a 12·5 cm. Swedish filter, and with ammonia water (1 of ammonia 0·880 specific gravity ammonia liquor to 8 of water) wash the precipitate into the filter.

Wash six times with ammonia water as above.

Test the last washings with acidulated silver nitrate (see p. 381).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry thoroughly on the hot plate.

Place the dried filter and contents in a tared platinum or porcelain capsule and proceed to ignite. The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be

white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper.

During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule and contents and place in a desiccator to cool.

Weigh, and calculate.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus.

When 5 grammes of sample are operated on, the factor for ascertaining the percentage is—

$$\frac{27{\cdot}838}{5} = 5{\cdot}568.$$

Log 5·568 = 0·7456992.

EXAMPLE—

Weight of capsule + ash + precipitate	=	16·3348
„ capsule	=	16·3242
„ ash and precipitate . .	=	0·0106
„ filter ash	=	0·0008
„ precipitate ($Mg_2P_2O_7$). .	=	0·0098

$0{\cdot}0098 \times 5{\cdot}568 = 0{\cdot}0546.$

And 0·055 = percentage of phosphorus in the sample of steel.

Estimation of Phosphorus in Steels containing Arsenic.

From oxidised solutions of steel which contained arsenic and phosphorus the molybdate solution can precipitate compounds of both together.

The late Mr. Walter G. M'Millan pointed out that the presence of 0·01 per cent. of arsenic, if converted into the yellow molybdate precipitate, would calculate out in round numbers as 0·004 per cent. of phosphorus.*

By Prof. Eggertz' method ammonia-phospho-molybdate precipitate free from arsenic may be obtained by precipitating at 40° C., and allowing the precipitate four hours to settle out. The precipitation is not, however, always complete at 40° C. At higher temperatures arsenic is precipitated.

John E. Stead, F.R.S., pre-precipitates the arsenic as sulphide, filters off the solution containing the phosphorus, and in the concentrated filtrate precipitates the phospho-molybdate in boiling solution. His instructive details are, by kind permission, appended.†

Method for the Determination of Phosphorus.

By J. E. Stead.

The method employed for the determination of phosphorus is that known by the name of "The Molybdic Acid Process," in which the phospho-

* *Iron and Steel Institute Journal*, vol. i., 1895, p. 139.

† Report of International Committee submitted to the New York meeting of the Iron and Steel Institute, October, 1904.

molybdate of ammonia after precipitation is weighed and the amount of phosphorus calculated from the weight obtained.

In practice we use two modifications of this method, one in which the steel is dissolved in nitric acid (1·20 sp. gr.), solution decolourised by permanganate of potash, and after the addition of a sufficient quantity of nitrate of ammonia the phosphorus is precipitated with molybdate of ammonia, and the precipitate weighed on a tared filter-paper. This system is very useful for steels containing practically no arsenic and silicon.

In the other method precautions are taken to separate any arsenic which might be present.

4·89 grammes of the steel are dissolved in 35 c.c. of nitric acid of 1·42 specific gravity, and 25 c.c. of hydrochloric acid. The solution is evaporated to dryness, taken up with hydrochloric acid, a little water is added, and afterwards pure granulated zinc in quantities sufficient to completely reduce the ferric chloride to ferrous chloride. When the excess of zinc is dissolved, a few drops of ammonium sulphide are added and the solution is violently agitated. If the black sulphide of iron is not completely dissolved, a little more hydrochloric acid must be added until solution is effected. Sulphide of arsenic precipitates at once and coagulates on shaking, and may be filtered off after vigorous agitation or after standing overnight. After filtering, the residue contains the silica and sulphide of arsenic, the filtrate the phosphorus. The filtrate is oxidised with nitric acid after boiling

off the free sulphuretted hydrogen, and the bulk of liquid is reduced to about 70 c.c. by evaporation. After cooling by placing the beaker in cold water, strong ammonia is added until the solution is just neutral, then 8 c.c. of the same ammonia in excess. Nitric acid is now added until the hydrated oxide of iron has just passed into solution, and a final addition of 5 c.c. nitric acid is added. If the volume of liquid is greater than 100 c.c. it may be evaporated until reduced to that bulk. When boiling, 20 c.c. of a 10 per cent. solution of molybdate of ammonia in water* are added, and the beaker with contents well shaken and allowed to stand on the table to allow the phospho-molybdate of ammonia to completely separate. When the supernatant liquid is perfectly bright, and the precipitate has settled to the bottom, the solution is filtered through tared filter-papers. These latter are made in the following manner, viz.:—Two folded papers, after thoroughly drying in a water oven, are placed on opposite pans of an accurately adjusted balance. From the heavier paper portions are clipped off the apex until one filter counterpoises the other. They are then returned to the water oven for fifteen to twenty minutes They are then taken out, and final and accurate adjustment made. The whole filter is placed inside the other, and in this the precipitate is collected.

After washing the precipitate with water containing 1 per cent. nitric acid, it is given three

* Please note that this solution differs from the one directed to be used for other phosphorus estimations.

washings with distilled water. The filter with contents is then dried at about 110° C.

After drying thoroughly, the filters are separated, the counterpoise paper being placed on one pan, and the paper with precipitate on the other. Weights are added to the pan with the counterpoise paper until equilibrium is established. The weight thus obtained divided by three gives the exact percentage of phosphorus present in the original metal.

ESTIMATION OF MANGANESE IN STEEL.

Gravimetric Method.

Outline of the Process.—The weighed sample of the steel is dissolved, and the excess acid is carefully neutralised. A large quantity of water and a measured amount of ammonium acetate solution are added. On boiling, a bulky precipitate consisting of basic hydrate and acetate of iron is formed, and the solution containing the manganese is separated on filtering and washing. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, manganese hydrate is precipitated. This is collected, washed, and ignited. The percentage of manganese is ascertained from the weight of the finished residue of Mn_3O_4.

This method of estimating manganese has been objected to on the ground that the ignited precipitate may vary in composition. With care this need not be so, and the process, as here detailed, is regularly employed in leading iron and steel works for the estimation of manganese in steels, spiegel-eisen, and ferro-manganese. A process which yields concordant results over such a wide range—results acceptable alike to buyers and sellers—cannot consistently be classed as unreliable.

Details of the Process.—Weigh off 2 grammes of the sample. Transfer the weighed portion to a 1,200 c.c. (about 40-oz.) globular Bohemian flask.

Add 15 c.c. of 1·42 specific gravity nitric acid along with 7 c.c. of water. Prof. Arnold recommends hydrochloric acid for dissolving tool steel.

Set the flask on a hot plate to hasten solution.

When the sample has dissolved add about 20 c.c. of hot water, and boil.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid even after violent shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 35 c.c. of ammonium acetate solution (see p. 162).

From this point the process is also applicable to the gravimetric estimation of manganese in pig iron.

Boil briskly over the flame of a 16 mm. (about $\frac{5}{8}$-inch) Bunsen burner. If the Bohemian flask is set on a tripod, the top of which is of stout iron wire, the contents may be boiled over a large Bunsen flame, no gauze being required. When the top of the tripod has sharp edges such procedure is risky.

Prepare a 28 cm. (about 11-inch) folded filter of No. 598 C. S. and S. or other thick filter-paper, place it in an 18 cm. (about 7-inch) funnel, saturate it with hot water, and place it in a large

filter stand—see Fig. 7. Set under it a 1,200 c.c. (about 40-oz.) Phillips' conical beaker on a dry cork mat.

Allow the *boiling* to continue for about half a minute. If the liquid nearly froths over, remove the flask till the brisk action ceases, replace on the tripod, and allow the rapid boiling to continue. It

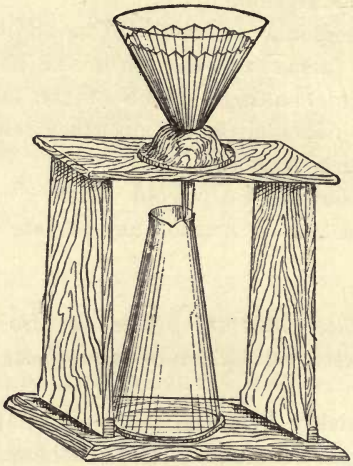

Fig. 7.—Stand, &c., for large funnel.

may be necessary to remove and replace two or three times. A voluminous brown or chocolate-coloured precipitate should be formed, from which a clear colourless liquid should drain away quickly when on the filter.

Immediately the boiling has finished, pour the contents of the flask on to the prepared filter, taking

care not to rest the neck of the hot flask on the edge of the glass funnel, or the former may crack.

Rinse the flask twice with hot water and pour the rinsings on to the filter. Allow the liquid to drain off thoroughly into the beaker flask.

Wash three times with hot water, collecting the washings in the beaker flask. If the operations have proceeded smoothly, filtering and washing may easily be completed within an hour.

Cool the filtrate and washings.

Add about 4 c.c. of bromine to peroxidise the manganese. Stir well while adding the bromine, and until it is all dissolved. The rubber tip of the stirring rod must be kept from contact with the drops of bromine, and should not be kept in the brominated liquid.

Allow to stand for about 15 minutes after brominating.

Cautiously add about 30 c.c. of strong ammonia solution.

Stir well, and allow to stand for a few minutes.

Boil till most of the excess ammonia has been driven off. Boiling hastens the precipitation of hydrated manganese peroxide, and filtering is facilitated by driving off the excess ammonia.

Filter through a 12·5 cm. Swedish filter-paper, and wash four times with hot water.

Place the funnel containing the filter-paper and precipitate on a dryer on a hot plate (see Fig. 4, p. 14), and allow to remain till dried.

Ignite the dried paper and precipitate in a tared platinum or porcelain crucible in a muffle furnace

which is at a white heat. Allow to remain in the hot muffle for 30 minutes at least.

Allow to cool in a desiccator, weigh, and note the weight.

Correction for Co-precipitated Iron.

A small quantity of ferric oxide usually accompanies the manganese oxide, and may be easily estimated by colour, in the following manner:—

Transfer the weighed substance to a 60 c.c. (about 2-oz.) Bohemian beaker.

Add about 10 c.c. of hydrochloric acid, and boil till the precipitate has dissolved.

Add about 5 c.c. of a 10 per cent. ammonium sulpho-cyanide solution.

If the mixture shows only a faint colouration, no correction is necessary.

If the mixture shows a decided colour, add about 10 c.c. of cold water, and pour the solution into a 100 c.c. stoppered graduated cylindrical measure. Rinse the beaker, and pour the rinsings into the measure. Mix well.

Measure 20 c.c. of standard iron solution (= 0·0005 gramme of ferric oxide, see p. 408) into a corresponding stoppered graduated glass having a distinguishing mark. Add 5 c.c. of the 10 per cent. sulpho-cyanide solution, and mix well.

Compare the depth of colour of the solutions.

Dilute the more highly-coloured solution, so as to bring each to the same depth of colour.

Calculate the weight of the co-precipitated ferric oxide, thus—

Divide the weight of ferric oxide in the standard solution by its volume, and multiply the product by the volume of the solution of the oxides from the manganese estimation.

EXAMPLE.—Fe_2O_3 in standard solution = 0·0005 gramme diluted to 25 c.c.

Solution of oxides diluted to 40 c.c.

$$\frac{0{\cdot}0005}{25} = \times\ 40 = 0{\cdot}0008.$$

0·0008 = weight of co-precipitated ferric oxide.

Calculate the percentage of manganese.

On igniting the precipitate as directed, the manganese peroxide is converted into Mn_3O_4. Mn_3O_4 contains 72·052 per cent. of manganese, and when 2 grammes of sample have been operated on the factor for calculation is

$$\frac{72{\cdot}052}{2} = 36{\cdot}026.$$

EXAMPLE—

	Gramme.
Weight of $Mn_3O_4 + Fe_2O_3$ + filter ash	= ·0164
„ filter ash	= ·0008
„ $Mn_3O_4 + Fe_2O_3$ . . .	= ·0156
„ Fe_2O_3	= ·0008
„ Mn_3O_4	= ·0148

0·0148 × 36·026 = 0·53 = percentage of manganese in the sample of steel.

Log 36·026 = 1·5566160.

Estimation of Manganese in Steel.

Colorimetric Method

suggested by Mr. Hugh Marshall. Details of process by Mr. Harry E. Walters, Duquesne Steel Works.*

Outline of the Process.—When steel containing manganese is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour is developed, the depth of which depends on the amount of manganese present. This is compared with the colour from an equal weight of steel containing a known percentage of manganese.

Details of the Process.—Weigh off a suitable quantity of the sample. If the steel is supposed to contain 0·75 per cent., or over, 0·1 gramme should be taken; if the supposed percentage is less, 0 2 gramme should be weighed off.

Transfer the weighed portion to an 18 × 1·6 cm. (about 7 × $\frac{5}{8}$ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add to each 10 c.c. of nitric acid of 1·2 specific gravity. If 0·1 gramme of steel has been taken, 6 c.c. of nitric acid will suffice.

Place the test tubes in a water bath (see Fig. 6, p. 21), and heat until the steels have dissolved and all nitrous fumes are driven off.

Add 15 c.c. (or 10 c.c. for 0·1 gramme of steel) of a 0·133 per cent. solution of silver nitrate (= 0·02

* Proceedings of Engineers' Society of Western Pennsylvania.

gramme of $AgNO_3$ in 15 c.c.). This will cool the solution to the temperature at which the next reagent should be added.

Immediately add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 163).

Continue heating in the water bath till oxidation commences, then for about half a minute longer.

Remove the tubes from the bath while the evolution of gas continues, and place them in a cold-water bath

When the solutions have cooled, transfer the coloured solution from the standard steel to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer the coloured solution from the other steel to a corresponding Eggertz' tube, and compare with the standard solution.

> NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker coloured solution with cold distilled water as far as necessary, mix well and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage of manganese in the standard steel by the volume of its solution, and multiply the product by the volume of the solution of the steel which is being tested.

EXAMPLE.—Standard steel contained 0·52 per cent. of manganese, and the solution was diluted to 20·8 c.c. The solution from the sample of steel being tested required to be diluted to 23·2 c.c.

Then $$\frac{0{\cdot}52}{20{\cdot}8} \times 23{\cdot}2 = 0{\cdot}58,$$

and 0·58 = percentage of manganese in the sample of steel.

ESTIMATION OF SULPHUR IN STEEL.

Evolution and Gravimetric Method.

Outline of the Process.—The weighed sample is placed in a properly-fitted evolution flask, and acid is added so as to cause the sulphur to be converted into sulphuretted hydrogen, which, as it bubbles through a solution of copper sulphate, forms a precipitate of copper sulphide. The sulphide is separated on a filter, washed thoroughly, dried, ignited, and the residue weighed.

The reactions may be conveniently summarised in the following equations, when R = Mn or Fe:—

$$RS + 2HCl = RCl_2 + H_2S.$$
$$H_2S + CuSO_4 = CuS + H_2SO_4.$$

The washed and dried copper sulphide, on being strongly heated with access of air, is oxidised.

$$2CuS + 3O_2 = 2CuO + 2SO_2.$$

From the weight of the copper oxide the quantity of sulphur which was present is deduced.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask which has been fitted with a rubber cork carrying a safety funnel, condenser, and delivery tube arranged as shown in Fig. 8 (see next page).

Moisten the cork, and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of cold saturated solution of copper sulphate into a 7-inch × 1-inch (18 × 2·5 cm.) test tube or beaker.

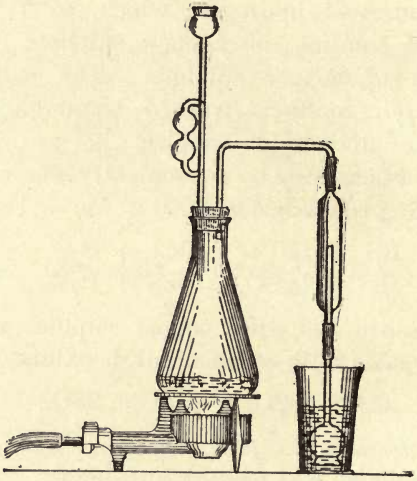

Fig. 8.—Flask, &c., for sulphur evolution.

Arrange the apparatus so that the condensing delivery tube dips into the solution.

Pour about 40 c.c. of 1·16 specific gravity pure hydrochloric acid into the safety funnel.

If necessary, lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of acid into the flask.

A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the burner—still permitting the gases to come off through the copper sulphate solution—and allow to remain there until all the steel has dissolved, and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube.

Filter off the copper sulphide, using a 12·5 cm. Swedish (but not an "ashless") filter.

Wash any adhering sulphide from the delivery tube on to the filter.

Wash the copper sulphide about twelve times with hot water. This precipitate should be washed quickly. It is difficult to wash all the copper sulphate through an ordinary filter; it is more difficult to wash it from an "ashless" filter.

Dry the precipitate and filter.

Ignite in a tared porcelain capsule, at first gently in a muffle, and then for 30 minutes in a moderately hot part of the muffle.

Allow the crucible and contents to cool in a desiccator.

Weigh, and calculate the percentage of sulphur in the steel.

EXAMPLE.—Weight of sample taken = 5 grammes.

Weight of capsule + ash + precipitate	= 8·3143
„ capsule	= 8·3070
„ ash + precipitate . .	= 0·0073
„ ash	= 0·0008
„ precipitate . . .	= 0·0065

Atomic weight of sulphur = 32·06.
Molecular weight of CuO = 63·6 + 16 = 79·6.

$$\frac{32{\cdot}06}{79{\cdot}6} = 0{\cdot}402764.$$

0·402764 = weight of S deduced from weight of CuO.

The factor for 5 grammes is

$$\frac{100}{5} \times 0{\cdot}402764 = 8{\cdot}0553.$$

Weight of ignited precipitate = 0·0065.

0·0065 × 8·055 = 0·052 = percentage of sulphur in the sample of steel.

It is not unusual to make a duplicate estimation on either 4 or 6 grammes.

Factor for 4 grammes = 10·07.
„ 6 „ = 6·71.

Estimation of Sulphur in Steel.

Volumetric (Iodine) Method.

Outline of the Process.—The sulphur is evolved as sulphuretted hydrogen, which is caught in a solution of caustic soda or caustic potash. This is afterwards more than neutralised with sulphuric acid, and titrated with standard iodine solution, starch being used as an indicator.

The changes which take place are:—

(1) The sulphur present, as sulphide, combines with hydrogen of the acid used for dissolving the steel, and sulphuretted hydrogen is evolved.

(2) The sulphuretted hydrogen is caught in caustic alkali solution, and held there as alkaline sulphide.

(3) On the caustic liquid being acidified, sulphuretted hydrogen is again formed, and is retained in the solution.

When R = Mn or Fe the reactions may be thus expressed:—

$$(1)\ RS + 2HCl = RCl_2 + H_2S.$$
$$(2)\ H_2S + 2NaHO = 2H_2O + Na_2S.$$
$$(3)\ Na_2S + H_2SO_4 = Na_2SO_4 + H_2S.$$

The quantity of sulphur present is then estimated as a result of the reaction:—

$$H_2S + I_2 = 2HI + S.$$

Addition of iodine in excess of that required for the completion of the reaction gives a permanent blue colour with starch solution.

STANDARDISING THE IODINE SOLUTION.—Having prepared the solutions, the iodine solution is standardised thus:—

Weigh off 5 grammes of steel drillings containing a known percentage of sulphur.

Transfer the weighed portion to a 300 c.c. (about 10-oz.) conical flask, which is fitted with a rubber cork carrying a safety funnel and a delivery tube.

Moisten the cork. and insert it in the neck of the flask.

Direct a jet of water between the cork and the curvature of the flask rim.

With a spiral motion press the cork firmly into the neck of the flask, so as to make a good gas-tight joint.

Pour about 50 c.c. of the prepared caustic soda solution (see p. 415) into a beaker or an 18 cm. × 2·5 cm. (about 7-inch × 1-inch) test tube.

Arrange the apparatus so that the condensing delivery tube dips into the solution, as shown in Fig. 8, p. 44.

Pour about 40 c.c. of pure 1·16 specific gravity hydrochloric acid into the safety funnel. Lessen the back pressure by momentarily raising the flask, &c., but not the test tube. This will facilitate the flow of the acid into the flask. A large quantity of gas, from the decomposition of carbide, is evolved along with the sulphuretted hydrogen. Slow evolution leads to a low result. The gases should be caused to come off at a fairly rapid rate.

When brisk action has subsided, pour 40 c.c. of hot water through the safety funnel into the flask.

When the action has somewhat slackened, light the

burner—still allowing the gases to come off through the caustic soda or potash solution—and allow to remain there until all the steel has dissolved and the solution in the flask has boiled for one or two minutes.

Detach the delivery tube, and rinse it into a 7-inch porcelain basin.

Empty the solution from the beaker or test tube into the same basin.

Wash the beaker or test tube, collecting the washings also in the basin.

Add 30 c.c. of dilute sulphuric acid (see p. 172) and about 5 c.c. of the freshly-prepared but cold starch solution (see p. 171).

From a burette filled to zero, carefully run standard iodine solution (see p. 166) into the basin while stirring briskly. When a decided violet colour appears which is somewhat persistent, add the iodine solution carefully drop by drop, and, when a distinct violet colour remains for about a minute after the addition of one of the drops, read off and note the volume of iodine solution used.

Correction for Quantity of Iodine Solution required to show Colour in the Solutions used.

Into a 7-inch porcelain basin put
About 50 c.c. of the caustic soda solution.
„ 30 c.c. of the dilute sulphuric acid solution.
„ 50 c.c. of cold, distilled water, and
„ 5 c.c. of the starch solution.

Run in, cautiously, standard iodine solution (stirring meanwhile), until a violet colour of the

same depth as in the other basin appears and remains.

Read off the quantity taken, and deduct from the quantity used in the former titration.

Duplicate the sulphur estimation, using 4 grammes of the steel.

If the results are fairly concordant, they may be accepted; if the difference is too great, make another estimation, using $4\frac{1}{2}$ grammes of the steel.

Calculation for Standardising.

5 grammes of the steel (which was known to contain ·046 per cent. of sulphur) required 9·4 c.c. of the standard iodine solution, and the blank experiment required 0·3 c.c.

∴ The H_2S from the steel required = 9·1 c.c.

$$\frac{0{\cdot}046 \times 5}{100} = 0{\cdot}0023.$$

$$\frac{0{\cdot}0023}{9{\cdot}1} = 0{\cdot}0002527 = \text{result of 1st estimation.}$$

7·43 c.c. (after correction for blank) of the standard iodine solution were required for 4 grammes of the steel.

$$\frac{0{\cdot}046 \times 4}{100} = 0{\cdot}00184.$$

$$\frac{0{\cdot}00184}{7{\cdot}43} = 0{\cdot}0002476 = \text{result of 2nd estimation.}$$

Result of 1st estimation = 0·0002527.
Result of 2nd estimation = 0·0002476.

Average of the two estimations = 0·0002502.

The bottle containing the solution is therefore labelled "Standard iodine solution: every c.c. = ·0002502 gramme of sulphur. Deduct for blank 0·3 c.c."

If the solution is kept in stock for a time, it should be restandardised before using again. If in regular use, restandardise every third day.

Estimation of Sulphur in a Sample of Steel by the Volumetric (Iodine) Method.

Weigh off 5 grammes of fine drillings taken through such a depth of the sample as required for a fair average.

Proceed exactly as in standardising.

Note the volume of the standard iodine solution required, and deduct the volume required for the blank.

Duplicate on 4 grammes

Calculate the results.

Example of Calculation.—5 grammes of the steel sample required 10·1 c.c. of the standard iodine solution.

The blank was ·33, therefore the standard iodine solution required for the sample steel was 9·77 c.c.

Every c.c. of the iodine solution = ·0002502 gramme of sulphur.

$$\frac{\cdot 0002502 \times 100 \times 9\cdot 77}{5} = \cdot 005004 \times 9\cdot 77 =$$

0·049 = percentage of sulphur in sample of steel.

Cadmium and Iodine Method.

Instead of using a solution of caustic soda, the evolved sulphuretted hydrogen may be caught in a solution of cadmium chloride prepared as directed on p. 404. Cadmium sulphide is precipitated, and is afterwards dissolved and estimated by titrating with standard iodine solution. The apparatus is fitted up as shown in Fig. 8 (p. 44), except that a larger beaker is employed to hold the 20 c.c. of 2 per cent. cadmium chloride solution and 200 c.c. of cold water. 5 grammes of the sample are treated with acid and water, and the gases evolved are led into the cadmium chloride solution. When evolution is complete, 10 c.c. of cold starch solution and 25 c.c. of 1·16 specific gravity hydrochloric acid are added to the contents of the beaker. For starch solution see p. 171.

When the whole is cold, standard iodine solution (see p. 166) is measured in till a permanent blue colour is obtained.

An advantage of this method is that one may, with practice, approximately gauge the percentage of sulphur in the sample before titrating.

The procedure, precautions, method of standardising, and calculating are all as described in the preceding pages.

At the National Physical Laboratory, Bushy Park, London, the volumetric estimation of sulphur is carried out thus:*—The steel drillings are dissolved in the evolution flask of this apparatus in hydrochloric acid of 1·10 specific gravity, the operation being aided

* Rosenhain, *Iron and Steel Institute Journal*, vol i., 1908.

by heat, although boiling the acid is avoided. The evolution flask and entire apparatus are filled, prior to the commencement of the operation, with an atmosphere of carbon dioxide, obtained by passing a stream of this gas, derived from a cylinder of liquid carbonic acid, through the entire apparatus. The evolved gases, aided towards the end of the operation by a further stream of carbonic acid, are bubbled through an absorption flask containing a solution of cadmium acetate strongly acidified with acetic acid (25 grammes pure cadmium acetate and 10 per cent. glacial acetic acid per litre); after passing this flask the gases pass through a narrow-bore tube of vitreous silica heated to redness by a Bunsen burner with a flat flame, the gases passing finally through a second cadmium acetate absorption flask and then away to the fume-chamber. When the steel has completely dissolved, the contents of the two absorption flasks are mixed and the yellow sulphide of cadmium is filtered off; this is a rapid operation since the flask need not be washed carefully—the operation is merely intended to separate the sulphide from the bulk of the absorption liquid. As soon as this has been done the precipitate is washed from the filter back into the original flask, and there dissolved in 10 c.c. of standard iodine solution, the action being aided by the introduction of a small quantity of hydrochloric acid. The excess of iodine is then titrated by means of sodium thiosulphate and starch. It is to be observed that while this titration can be carried out in the liquid of the absorption flasks without filtration, it has been found that this leads to occasional discrepancies in the

results. Apparently, particularly in the case of high-carbon steel, the evolved gases carry into the absorption flask something which is capable of absorbing iodine, but which is not sulphur; this disturbing substance can be eliminated by the filtration described above.

The following table, which contains typical examples from a wide range of steel, shows the closeness of the agreement observed between the results of this evolution method and the oxidation method:—

Steel.	Lab. No.	Percentage of Sulphur found by	
		Evolution.	Gravimetric.
Tyre, . .	896	0·042	0·044
Tyre, . .	936	0·046	0·049
Tyre, . .	952	0·045	0·049
Shaft, . .	...	0·041	0·043
Tyre, . .	969	0·014	0·013
Plate, . .	980	0·048	0·045
Joist, . .	1018	0·054	0·052
Joist, . .	1054	0·062	0·063

Estimation of Sulphur by Oxidation and Precipitation as Barium Sulphate.

Outline of the Process.—The weighed sample is dissolved in acid and oxidised. It is again dissolved, and, on addition of barium chloride solution, barium sulphate is precipitated. This is collected on a filter, washed, dried, and weighed. From the ascertained weight the percentage of sulphur is calculated.

Details of the Process.—Weigh off 3 grammes of the sample.

Transfer to a 3-inch × 1-inch platinum basin.

Add sufficient concentrated nitric acid, in small instalments, to dissolve the sample. Keep the basin covered with a watch-glass during the period of dissolving.

When completely dissolved, add 2 grammes of potassium nitrate.

Evaporate to dryness.

Ignite at a red heat.

When cool, add 50 c.c. of a 1 per cent. solution of sodium carbonate.

Gently boil for a few minutes.

Filter, collecting the filtrate (and washings) in a 7·5 × 5 cm. (about 3-inch × 2-inch) beaker.

Wash with hot 1 per cent. sodium carbonate solution.

Add hydrochloric acid to acidify the filtrate.

Evaporate to dryness.

When the beaker has cooled, add 5 c.c. of hydrochloric acid in 45 c.c. of water.

Boil briskly for five minutes.

Filter, collecting the filtrate (and washings) in a 10 × 7·5 cm. (about 4-inch × 3-inch) beaker.

Wash thoroughly with hot water containing about 2 per cent. of hydrochloric acid.

Add 5 c.c. of a 10 per cent. solution of barium chloride. This should precipitate all the sulphur as barium sulphate according to the equation—

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$

Filter through a close-texture filter-paper.

Wash well with hot water.

Test some of the last washings by collecting in a clean test tube, and adding a few drops of clear acidified silver nitrate solution.

Wash twice after all the chloride appears to have been washed out.

Dry the precipitate on the filter.

Ignite in a tared crucible for half an hour in a hot muffle.

Weigh and calculate.

EXAMPLE—

	Grammes.
Weight of crucible + ash + precipitate .	= 16·8504
„ crucible	= 16·8308
„ ash + precipitate . . .	= 0·0196
„ ash	= 0·0010
„ precipitate ($BaSO_4$) . .	= 0·0186

Percentage of S in $BaSO_4$ = 13·73.

$\frac{13{\cdot}73}{5}$ = 2·746 = factor when 5 grammes of sample are taken.

$$0{\cdot}0186 \times 2{\cdot}746 = 0{\cdot}051.$$

0·051 = percentage of sulphur in the sample of steel.

ANALYSIS OF PIG IRON.

ESTIMATION OF COMBINED CARBON.

EGGERTZ' COLORIMETRIC METHOD.

Outline of the Process.—This method is based on the fact that when iron which contains carbon in a certain state of combination is dissolved in dilute nitric acid, a yellow-coloured solution is obtained, and the depth of the colour is, within limits, in proportion to the amount of carbon present in that state of combination.

In practice a weighed quantity of a standard steel is dissolved, the solution diluted to a definite volume in a graduated Eggertz' tube, and mixed well. A like quantity of the sample of pig iron to be tested is dissolved and filtered, and the filtered solution is carefully diluted in a corresponding graduated tube till the solution shows the same depth of colour. A short calculation then gives the percentage.

Details of the Process.— Weigh off 0·1 gramme of a suitable standard.

> **As a standard, steel is preferable to pig iron, even against the well-founded belief that steel should be tested against steels of their own class.**

Suitable standards:—

For	**Grey iron,**	**0·50 per cent. carbon steel.**	
„	**Mottled iron,**	**1·00**	**„**
,	**White iron,**	**1·40**	**„**

Transfer the weighed portion to a clean, dry 13 × 1·3 cm. (5 inches × ½ inch) test tube with a distinctive label or mark on it. A rubber ring makes a suitable distinction for the standard tube.

Weigh off 0·1 gramme of the sample of pig iron to be tested.

Transfer the weighed portion to a similar test tube with a distinctive label or mark on it.

To each weighed quantity add nitric acid solution of 1·2 specific gravity.

If 0·5 standard,	**. . .**	**2 c.c.**
„ 1·0 „	**. . .**	**2·5 c.c.**
„ 1·4 „	**. . .**	**3·0 c.c.**

When brisk action has ceased, set the test tubes, with contents, in a bath of boiling water, and keep at boiling point for twenty minutes. The rack and stand shown in Figs. 1 and 2 (pp. 3 and 5) are convenient.

Withdraw the test tubes from the hot bath.

Immediately filter the solution from the pig iron through a 7 cm. filter into a 20 c.c. Eggertz' tube. Rinse the test tube with warm water, collecting the washings, through the filter, in the same Eggertz' tube.

If the solution is not promptly filtered, as directed, a coloured precipitate may settle out and spoil the estimation.

Label the Eggertz' tube.

Allow to cool.

Drain the cold standard solution from the test tube into a corresponding Eggertz' tube, which has a distinguishing mark, such as a rubber ring or a mark made with a diamond. Rinse into the Eggertz' tube with a fine jet of cold water.

Make up to a definite measure with cold water.

Close the graduated tube, and shake it so as to thoroughly mix the fluids.

Compare the depth of colour of the two solutions.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through ground glass or a sheet of moistened filter-paper will pass through the solutions. Change the relative positions of the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute the darker-coloured solution with cold water, mix well, and compare again.

If necessary, dilute further, mix, and compare.

Repeat until the solution from the sample is of the same depth of tint as that of the standard.

When the solutions in the Eggertz' tubes are of the same depth of colour, read off the volumes of the solutions, and calculate the result.

EXAMPLE.—Standard material contained 0·63 per cent. of combined carbon; solution was diluted to 6·3 c.c.

Sample required to be diluted to 7·8 c.c.

∴ Combined carbon in the sample of pig iron = 0·78 per cent.

For other examples of calculations, see pp. 7 and 8.

ESTIMATION OF GRAPHITIC CARBON IN PIG IRON.

Outline of the Process.—To the weighed sample in a beaker acid is added and evaporated to dryness. During the evaporation the silicon is oxidised to silica. Acid is again added, and, after boiling for a few minutes, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The washed residue is transferred to a tared basin, dried on a steam bath, and the weight ascertained. On ignition, the graphite is burned off, and, after cooling, the fixed residue is weighed. The weight of the graphite is found by difference, and the percentage is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12·5 × 9·7 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 30 c.c. of 1·16 specific gravity hydrochloric acid.

Evaporate on a hot plate till the residue in the beaker is quite dry (see note on "hot plate," p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of hot water and 15 c.c. of 1·16 specific gravity hydrochloric acid.

Boil until the iron has dissolved.

Filter through a 12·5 cm. Swedish filter.

Wash three times with acidulated water—1 of 1·16 specific gravity hydrochloric acid to 6 of water.

Wash three or more times with hot water.

Allow to drain thoroughly.

With a fine-jet wash bottle wash the insoluble matter from the filter into a tared platinum or porcelain basin of 7·6 cm. (or about 3 inches) diameter.

Evaporate on a water bath, and complete the drying in a steam oven.

Allow to cool in a desiccator.

Weigh and note the weight.

Ignite the residue. Let the basin remain in the muffle until a pure white, or faintly pink or reddish, residue is left. The residue (silica) should be white, but even a slight trace of iron will impart a colour.

Withdraw the basin and contents, and allow to cool until the basin can be lifted by hand.

Complete the cooling in a desiccator.

Weigh again and calculate.

EXAMPLES.—

(*a*) When the percentage of silicon is not required.

	Grammes.
Weight of capsule + residue, before ignition, ...	= 27·4374
Weight of capsule + residue, after ignition, ...	= 27·3850
Loss on ignition = weight of graphite	0·0524

2 grammes of sample were taken for estimation.

$$\frac{100}{2} \times \cdot 0524 = 2 \cdot 62.$$

2·62 = percentage of graphite in the sample of pig iron.

(*b*) When the percentage of silicon is required.

EXAMPLE—

	Grammes.
Weight of basin + insoluble matter, after drying, . .	= 27·4374
Weight of basin	= 27·3185
Weight of insoluble matter, after drying (*graphite and silica*), .	= 0·1189

	Grammes.
Weight of basin + insoluble matter, after ignition, . .	= 27·3850
Weight of basin	= 27·3185
Weight of insoluble matter, after ignition (*silica*), . . .	= 0·0665

	Grammes.
Weight of insoluble matter, before ignition, ...	= 0·1189
Weight of insoluble matter, after ignition, ...	= 0·0665
Loss on ignition (*graphite*) . .	= 0·0524

To find percentage of graphite (2 grammes taken)—

$$\frac{100}{2} \times \cdot 0524 = 2 \cdot 62.$$

2·62 = percentage of graphite.

To find percentage of silicon:—

The ignited pure residue (SiO_2) contains 47·02 per cent. of silicon, and when 2 grammes of sample are operated on, the factor for calculation is

$$\frac{47 \cdot 02}{2} = 23 \cdot 51.$$

EXAMPLE—

	Grammes.
Weight of silica + crucible	= 18·2783
„ crucible . .	= 18·2118
„ silica . .	= 0·0665

0·0665 × 23·51 = 1·56 = percentage of silicon in the sample.

Log 23·51 = 1·3712526.

Estimation of Total Carbon in Pig Iron.

(*a*) Add together the percentage of combined carbon and of graphitic carbon; or

(*b*) Estimate by combustion.

ESTIMATION OF SILICON IN PIG IRON.

If it is intended to estimate silicon, phosphorus, and manganese in the sample of pig iron, the method described on pp. 74 to 77 should be adopted, but when silicon alone is to be determined the following method is recommended.

Outline of the Process.—When pig iron is dissolved in acid and the solution is evaporated to thorough dryness, the silicon (Si) becomes oxidised to silica (SiO_2). After boiling for a few minutes in hydrochloric acid, the insoluble residue from an ordinary pig iron consists of silica and graphite only. These are separated from the soluble constituents by filtering and washing. The insoluble residue is collected on a filter, washed, dried, ignited till all the graphite has been burned off, and weighed. The percentage is then calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12·2 × 9·7 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p. 149) till the residue in the beaker is quite dry, then allow to stand on the hot plate for about ten minutes more to complete the oxidation of the phosphorus.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of 1·16 specific gravity hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter the solution through a 12·5 cm. Swedish filter-paper.

Wash the residue (silica and graphite) well, first with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 6 of water—and afterwards with hot water as often as required.

All traces of colour should be removed from the filter-paper and the precipitate. If washing does not effect this, the residue must be afterwards purified by fusion (see p. 16) **or treated with hydrofluoric acid, which causes the volatilisation of silica** (see next page).

Dry the residue by placing the funnel with filter-paper and contents on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents. and allow to cool in a desiccator.

Weigh quickly and note the weight.

Examine the weighed residue.

If the residue is white, calculate the percentage of silicon in the sample.

If, as sometimes happens, the silica is not quite white, add a few drops of hydrofluoric acid to the contents of the weighed platinum capsule (this must not be done in a porcelain capsule or crucible), carefully evaporate, ignite, allow to cool in a desiccator, and re-weigh.

The percentage of silicon in silica is 47·02, and when 2 grammes of sample are taken for the estimation, the factor for calculating the percentage is—

$$\frac{47{\cdot}02}{2} = 23{\cdot}51.$$

Log 23·51 = 1·3712526.

EXAMPLES.—

(*a*) Without the use of hydrofluoric acid.

	Grammes.
Weight of capsule + silica + ash	= 19·1458
„ capsule . . .	= 19·0685
„ silica + ash . .	= 0·0773
„ filter ash . . .	= 0·0008
„ silica	= 0·0765

$$0{\cdot}0765 \times 23{\cdot}51 = 1{\cdot}799.$$

1·80 ≒ percentage of silicon in the sample of pig iron.

(*b*) Using hydrofluoric acid.

	Grammes.
Weight of capsule + contents, .	= 18·7243
Weight of capsule + impurities after treatment with hydrofluoric acid	= 18·6913
	0·0330
Add for impurity in the hydrofluoric acid, the amount of which had been previously ascertained in a like quantity of the acid .	= 0·0010
Weight of residue volatilised = *silica*	= 0·0340

Then using the factor (23·51) noted in example (*a*),

$$0{\cdot}034 \times 23{\cdot}51 = 0{\cdot}799.$$

0·80 $\doteqdot$ percentage of silicon in the sample of white pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

STANDARD METHOD—APPLICABLE TO ALL PIG IRONS EXCEPT SWEDISH AND HEMATITE.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron, except graphitic carbon and silicon, are dissolved and are separated from the insoluble residue (which may be used to ascertain the percentage of silicon) by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound $[(NH_4)_3PO_4 . 12MoO_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the iron. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12·2 × 9·6 cm. (about $4\frac{3}{4}$ × $3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149), then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid add 20 c.c. of hydrochloric acid and evaporate to about half bulk.

Add about 20 c.c. of hot water, and boil for two minutes.

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 300 c.c. (about 10-oz.) conical flask.

Wash three times with dilute hydrochloric acid—1 of 1·16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. **Silicon may be estimated in the residue.**

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium-nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution and pour, all at once, 175 c.c. of molybdate solution (see p. 162) down the thermometer into the flask.

175 c.c. should be sufficient for a pig iron containing 3 per cent. of phosphorus. For a forge or foundry pig iron 100 c.c. should be enough.

This will cause the formation of a yellow precipitate containing all the phosphorus.

Shake the flask well, and allow the precipitate to settle.

Filter the solution through a 12·5 cm. close-texture filter-paper, collecting the filtrate (and washings) in a beaker.

Wash, once by decantation and afterwards in the usual way, with nitric acid solution—1 of acid (specific gravity, 1·42) to 20 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 500 c.c. beaker.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (·880 specific gravity) to 8 of water—collecting the solution in the beaker.

Wash four times with dilute ammonia solution and twice with warm water. Collect the washings in the same beaker as the solution. Heat the solution and washings to about 60° C.

Add one-sixth bulk of ammonia liquor (0·88 specific gravity).

Add 25 c.c. of magnesia mixture (see p. 167), and stir well.

Allow the precipitate to settle.

Filter, using a 12·5 cm. Swedish filter-paper.

Wash with dilute ammonia solution—1 of am-

monia liquor (specific gravity, 0·88) to 8 of water—until the washings are free from chlorides.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The residue should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses ammonia and water, and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus—

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule, or crucible, and its contents and allow to cool in a desiccator.

Weigh, and note the weight.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus. When 2 grammes of sample have been operated on the factor for calculation is—

$$\frac{27{\cdot}838}{2} = 13{\cdot}919.$$

$$\text{Log } 13{\cdot}919 = 1{\cdot}1436080.$$

EXAMPLE—

	Grammes.
Weight of precipitate + filter ash + capsule	= 19·9607
„ capsule	= 19·7385
„ precipitate + ash . . .	= 0·2222
„ ash	= 0·0008
„ precipitate	= 0·2214

$$0{\cdot}2214 \times 13{\cdot}919 = 3{\cdot}08.$$

3·08 = percentage of phosphorus in the sample of pig iron.

ESTIMATION OF PHOSPHORUS IN PIG IRON.

RAPID METHOD—NOT APPLICABLE TO SWEDISH OR HEMATITE PIG IRONS.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron — except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings are collected in a 250 c.c. flask, cooled, and made up to definite volume. A measured quantity of solution is withdrawn by a pipette, and transferred to a flask. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the

measured quantity, is collected, washed, dried, and weighed.

Details of the Process.—Weigh off ·2 grammes of the sample in the form of drillings or fine turnings.

Transfer the weighed portion to a 12·2 × 9·6 cm. (about $4\frac{3}{4} \times 3\frac{3}{4}$ inches) Bohemian or Jena beaker.

Add 15 c.c. of hydrochloric acid of 1·16 specific gravity along with 15 c.c. of nitric acid.

Evaporate on a hot plate (see p. 149) to dryness, then allow to stand on the hot plate for ten minutes more to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack on contact with liquid, add 20 c.c. of 1·16 specific gravity hydrochloric acid, and evaporate to about half bulk.

Add 25 c.c. of hot water, and boil for two minutes.

If it is desired to estimate silicon in the washed residue:—

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate and washings in a 250 c.c. flask.

Wash three times with dilute hydrochloric acid, say 1 of 1·16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper, and the washings are colourless. With ordinary care the residue can be completely washed without making the volume more than 250 c.c.

Cool the solution, make up to the mark with cold water, and mix well.

If it is not desired to estimate silicon in the washed residue :—

Wash the solution out of the beaker (without filtering) into a 250 c.c. flask.

Cool under a water tap.

Make up to the mark with cold water.

Mix well and allow to settle.

Withdraw from the clear portion of the solution, by means of a pipette, the quantity required for the phosphorus estimation ; or, if the results are required earlier, the measured portion from the pipette may be run through a filter and washed into the precipitating flask.

In either case—

Draw from the 250 c.c. flask enough of the solution to fill the pipette to the mark indicating the quantity which will deliver 20·38 c.c. This is done to clean it. Reject the solution as it runs out.

Draw from the 250 c.c. flask more of the solution into the pipette, and adjust it to the 20·38 c.c. delivery mark.

Run the measured quantity into a 200 c c. (about 7 ozs) conical flask.

Add 2 c.c. of ammonia liquor.

Neutralise with hydrochloric acid.

Add 17 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution, and add all at once 20 c.c. of molybdate solution (see p. 162), which may be poured down the

lower part of the thermometer into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for one minute or more. While shaking, press the forefinger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate on to a 9 cm. close-texture, smooth-surface filter-paper. Wash any remaining precipitate on to the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1·42 specific gravity acid to 50 of water.

Open out the filter-paper, and, with a fine-spout wash bottle containing warm water, wash the precipitate into a tared porcelain basin or a tared basin of platinised nickel (see note on p. 150).

Evaporate on a water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

Other plans are (*a*) to use counterpoised filter-papers, and (*b*) to brush the dried precipitate on to a tared watchglass, and weigh.

The yellow precipitate, when thoroughly dried on a water bath, contains 1·63 per cent. of phosphorus.

When the solution from 2 grammes is made up to 250 c.c., 20·38 c.c. = 0·163 gramme, and when this

quantity has been used for the estimation, the factor for calculation is

$$\frac{1{\cdot}63}{0{\cdot}163} = 10.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate .	= 24·669
„ basin	= 24·568
„ precipitate, . .	= 0·101

$$0{\cdot}101 \times 10 = 1{\cdot}01.$$

1·01 = percentage of phosphorus in the sample of pig iron.

STANDARD METHOD FOR THE ESTIMATION OF PHOSPHORUS IN HEMATITE OR SWEDISH PIG IRONS.

MOLYBDATE AND MAGNESIA METHOD.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron, except graphitic carbon and silicon, are dissolved and are separated from the insoluble residue (which may be used to ascertain the percentage of silicon) by filtering and washing. To the filtrate, molybdate solution is added to cause the precipitation of a yellow compound $[(NH_4)_3PO_4 . 12MoO_3]$ containing all the phosphorus. The yellow precipitate is collected on a filter and washed, thus separating the phosphorus from the iron. The washed precipitate is dissolved in ammonia liquor and the solution is neutralised. Magnesia mixture is then added to precipitate the phosphorus as

magnesium-ammonium-phosphate, which is collected, washed, and dried. On ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed. From the weight of the precipitate the percentage of phosphorus in the steel is calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a $15 \times 11{\cdot}5$ cm. (about $6 \times 4\frac{1}{2}$ inches) Bohemian or Jena beaker.

Add 40 c.c. of 1·16 specific gravity hydrochloric acid along with 20 c.c. of 1·42 specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of 1·16 specific gravity hydrochloric acid and allow to boil until all the iron appears to be dissolved.

Add about 20 c.c. of hot water, and boil briskly for a few minutes more.

Filter through a 12·5 cm. Swedish filter-paper, collecting the filtrate (and washings) in a 250 c.c. conical flask.

Wash three times with dilute hydrochloric acid—1 of 1·16 specific gravity acid to 6 of water.

Wash with warm water until all traces of colour are removed from the filter-paper and the washings are colourless. **Silicon may be estimated in the residue.**

While stirring the filtrate, add ammonia solution to it until a permanent precipitate forms.

Dissolve the precipitate by cautiously adding nitric acid while stirring.

Add 35 c.c. of ammonium nitrate solution (see p. 163).

Heat to 90° C. Immediately raise the thermometer about 25 mm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 33 c.c. of molybdate solution (see p. 162) into the flask. This will cause the formation of a yellow precipitate containing all the phosphorus.

Cork the flask and shake it vigorously, so as to hasten the precipitation.

Allow to settle at a temperature under 100° C. for about fifteen minutes.

Pour the solution with the yellow precipitate into a 9 cm. close-texture filter, collecting the filtrate (and washings) in a beaker. Wash the remaining precipitate into the filter.

Wash the precipitate three times with very dilute nitric acid—1 of 1·42 specific gravity nitric acid to 50 of water.

Remove the beaker containing the filtrate, and place in its stead a clean 300 c.c. conical flask.

Dissolve the precipitate on the filter with dilute ammonia solution—1 of ammonia liquor (0·88 specific gravity) to 8 of water—collecting the solution (and washings) in the conical flask.

Wash four times with dilute ammonia liquor, and twice with warm water.

Heat the solution and washings to about 60° C.

Add 10 c.c. of 0·88 specific gravity ammonia liquor.

Mix the solutions in the flask.

Add, drop by drop, about 5 c.c. of magnesia mixture (see p. 167). Stir the solution briskly, or agitate the flask, while adding the magnesia mixture.

Cork the flask and shake it vigorously for about two minutes. (While shaking the flask, press the cork firmly to prevent its ejection.) This causes the formation of a finely crystalline precipitate of magnesium-ammonium-phosphate ($Mg(NH_4)PO_4 . 6H_2O$).

Allow the precipitate to settle for an hour or two.

Decant the clear solution through a 12·5 c.m. Swedish filter, and with dilute ammonia liquor wash the precipitate into the filter. Collect the filtrate (and washings) in a suitable beaker.

Wash six times with dilute ammonia liquor.

Test the last washings with acidulated silver nitrate (see p. 170).

Wash two or three times with the dilute ammonia liquor after all the chlorides have been washed out.

Dry the precipitate by placing the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14), covering with paper, and allowing to dry on the hot plate.

Place the dried residue and filter-paper in a tared platinum or porcelain capsule or crucible, and ignite.

The precipitate and filter should be thoroughly dried, and the ignition cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for

an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition the precipitate loses water and is converted into magnesium pyrophosphate = ($Mg_2P_2O_7$).

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

Withdraw the capsule or crucible and allow to cool in a desiccator.

Weigh, and calculate the result.

The percentage of phosphorus is calculated from the weight of magnesium pyrophosphate, which contains 27·838 per cent. of phosphorus.

When 5 grammes of sample are used for the estimation, the factor for ascertaining the percentage is

$$\frac{27{\cdot}838}{5} = 5{\cdot}568.$$

Log 5·568 = 1·7456992.

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 18·3536
„ capsule	= 18·3472
„ ash and precipitate . .	= 0·0064
„ filter ash	= 0·0008
„ precipitate ($Mg_2P_2O_7$) .	= 0·0056

$$0{\cdot}0056 \times 5{\cdot}568 = 0{\cdot}0312.$$

0·0312 = percentage of phosphorus in the sample of steel.

Rapid (Molybdate) Method for the Estimation of Phosphorus in Hematite or Swedish Pig Irons.

Outline of the Process.—The weighed sample is treated with acid, evaporated to dryness, and baked. On boiling the residue with acid, all the usual components of ordinary pig iron — except graphitic carbon and silicon—are dissolved, and are separated from the insoluble residue by filtering and washing. The filtrate and washings are collected and evaporated to small bulk. Ammonium nitrate is added to facilitate precipitation, and the whole is heated to a suitable temperature for precipitation by ammonium molybdate. The precipitate, which contains all the phosphorus in the measured quantity, is collected, washed, dried, cooled, and weighed.

In estimating phosphorus by this method, regard must be paid to the quantity, the degree of acidity, and the temperature of the solution when precipitating. The amount of ammonium nitrate in the solution has also an effect on the precipitation.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 15 × 11·5 cm. (about 6 × 4½ inches) Bohemian or Jena beaker.

Add 40 c.c. of 1·16 specific gravity hydrochloric acid along with 20 c.c. of 1·42 specific gravity nitric acid.

Evaporate on a hot plate to dryness (see note on hot plate, p. 149).

Allow the beaker to stand on the hot plate for ten minutes more, to complete the oxidation of the phosphorus to phosphoric anhydride (P_2O_5).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 35 c.c. of 1·16 specific gravity hydrochloric acid.

Boil until all the iron appears to be dissolved.

Add about 10 c.c. of hot water, and continue the boiling for about two minutes.

Allow the residue to subside, and pour the clear yellow liquid through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 9 × 7·5 cm. (about 3½ × 3 inches) Bohemian or Jena beaker.

Wash the residue into the filter.

Wash three times with water acidulated with 10 per cent. of 1·16 specific gravity hydrochloric acid.

Evaporate till the liquid is of the smallest possible bulk. If evaporation has been continued till some of the solution has dried on the glass, withdraw the beaker, and, when it has slightly cooled, gently pour one or more drops of hydrochloric acid on the spot, to dissolve the solidified matter. The beaker will then contain a concentrated and nearly neutral solution or syrup.

With a fine-spout wash-bottle containing warm water, wash the solution into a 150 c.c. (about 5-oz.) conical (Erlenmeyer) flask. Avoid dilution as much

as possible. The solution and washings should not measure more than 25 c.c.

Add 25 c.c. of ammonium nitrate solution (see p. 163).

Heat to about 90° C.

Immediately raise the thermometer about 2·5 cm. (about 1 inch) clear of the solution, and pour down the stem of the thermometer, all at once, 25 c.c. of molybdate solution (see p. 162) into the flask. This will cause the formation of a yellow precipitate containing the phosphorus.

Withdraw the thermometer, cork the flask, and shake it vigorously for about one minute. While shaking the flask, press the fore-finger on the cork to prevent its ejection.

Pour the solution with the yellow precipitate into a 9 cm. close-texture, smooth-surface filter-paper, collecting the filtrate (and washings) in a suitable beaker. Wash any remaining precipitate on the filter.

Wash the precipitate three times with very dilute nitric acid—1 of nitric acid (1·42 specific gravity) to 50 of water.

Open out the filter-paper, and, with a fine-spout wash-bottle containing warm water, wash the precipitate on to a tared porcelain basin or a basin of platinised nickel—see note on p. 150.

Evaporate on the water bath (Fig. 6, p. 21) till the precipitate is completely dried.

Wipe the basin and allow it to cool.

Weigh, and calculate the result.

The yellow precipitate, when thoroughly dried on

a water bath, contains 1·63 per cent. of phosphorus, and when 5 grammes of sample have been used for the estimation, the factor for calculation is

$$\frac{1{\cdot}63}{5} = 0{\cdot}326.$$

$$\text{Log } 0{\cdot}326 = \bar{1}{\cdot}5132176.$$

EXAMPLE—

	Grammes.
Weight of basin + precipitate	= 22·483
„ basin . . .	= 22·387
„ precipitate . .	= 0·096

$$0{\cdot}096 \times 0{\cdot}326 = 0{\cdot}313.$$

0·313 = percentage of phosphorus in the sample.

ESTIMATION OF MANGANESE IN PIG IRON.

Gravimetric Method.

Outline of the Process.—The weighed sample is treated with acid and evaporated to complete dryness. By this means the silicon is converted into insoluble silica. On the addition of more acid and the application of heat, the insoluble residue from an ordinary pig iron consists of silica and graphite only. The soluble portion is filtered off into a flask, and carefully neutralised. Ammonium acetate is added, and, on boiling, a bulky precipitate of ferric acetate and hydrate is formed. This is separated, by filtering and washing, from the liquid containing the manganese in solution. The manganese in the filtrate is peroxidised by the action of bromine.

On addition of ammonia, hydrated manganese oxide is precipitated. The precipitate is collected on a filter, washed, dried, and ignited. The percentage of manganese is calculated from the weight of the finished residue of Mn_3O_4.

Details of the Process.—Weigh off 2 grammes of the sample.

Transfer the weighed portion to a 12 cm. × 12 cm. (about $4\frac{1}{2}$ × $4\frac{1}{2}$ inches) Bohemian spouted beaker.

Add 15 c.c. of nitric acid, 1·42 specific gravity, along with 7 c.c. of hydrochloric acid of 1·16 specific gravity.

Evaporate on a hot plate till thoroughly dry (see note on hot plate, p. 149).

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add about 20 c.c. of nitric acid along with 10 c.c. of water, and set to boil briskly for a few minutes.

Filter the solution through a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 1,200 c.c. (about 40 ozs.) globular Bohemian flask.

Wash the residue (silica and graphite) three times at least with hot water.

Boil the filtrate and washings.

Add ammonia solution till a slight permanent precipitate forms and remains in the hot liquid, even after vigorous shaking. Much of the success of the estimation depends on the accuracy with which the neutralisation is effected.

Add about 600 c.c. of cold water.

Add 33 c.c. of ammonium acetate solution.

Then follow the details from the corresponding point on p. 35 to the end of the gravimetric process.

Estimation of Manganese in Pig Iron.

Colorimetric Method.

(From a Memo. by Percy Hill, Wednesbury.)

Outline of the Process.—When manganiferous pig iron in a fine state of division is dissolved in nitric acid, and silver nitrate and ammonium persulphate afterwards added, a pink colour appears, the depth of which depends on the amount of manganese present. The graphite and silica are allowed to settle, and a measured quantity of the clear pink-coloured solution is drawn off and transferred to a 50 c.c. Eggertz' tube. This is compared with the colour from an equal weight of pig iron containing a known percentage of manganese.

For pig irons containing under 1 per cent. of manganese, the colorimetric method for steels (see pp. 40 to 42) works satisfactorily if the graphite and silica are allowed to settle and 5 c.c. are drawn off for the estimation; but, if like quantities of solutions are used for pig irons containing over that percentage of manganese, a precipitate will separate out. This precipitation is avoided if Percy Hill's modification is adopted.

Details of the Process.—Weigh 0·1 gramme of the sample, which must be fine enough to pass through a 100-mesh sieve.

Transfer the weighed portion to an 18 × 1·6 cm. (about 7 × $\frac{5}{8}$ inch) test tube.

Weigh off an equal quantity of a suitable standard steel and transfer to a similar test tube.

Add 8 c.c. of nitric acid of 1·2 specific gravity to each.

Place the test tubes in a water bath (see p. 21), and allow them to remain until the iron has dissolved —generally about ten to fifteen minutes.

Add to each, 7·5 c.c. of 0·4 per cent. solution of silver nitrate.

Replace the test tubes with their contents in the water bath, and add to each about 1 gramme of previously moistened persulphate (see note on persulphate, p. 163).

Continue heating in the water bath until the colour appears, and, while the tubes are still effervescing, remove the tubes and place them in a cold-water bath.

When the solid residues in the tubes have subsided, draw off, with a pipette, 5 c.c. of the clear pink-coloured solution from the standard "pig" to a marked Eggertz' tube, make up with cold water to a suitable volume, and mix thoroughly.

Transfer a similar quantity of the coloured solution from the sample "pig" to a corresponding Eggertz' tube, dilute, and compare with the standard solution.

NOTE.—In comparing the tints, the graduated tubes are placed side by side, so that diffused light coming through the ground glass or a sheet of moistened filter-paper will pass through the solutions (see Fig. 2, and description of stand on pp. 5 and 6). Change the relative positions of

the tubes—standard tube to the right, and sample tube to the left, and *vice versâ*—during the comparison.

Dilute with cold distilled water as far as necessary, mix well, and compare again.

When the solutions in each tube agree in depth of colour, note the volumes, and calculate the percentage of manganese.

GENERAL RULE FOR CALCULATING.—Divide the percentage manganese of the standard pig iron by the volume of its solution, and multiply the result by the volume of the solution of the pig iron which is being tested.

EXAMPLE.—Standard pig iron contained 2·35 per cent. of manganese, and the measured portion of its pink-coloured solution was diluted to 23·5 c.c. A similar measure of the pink-coloured solution from the sample required to be diluted to 19·4 c.c.

$$\frac{2{\cdot}35}{23{\cdot}5} \times 19{\cdot}4 = 1{\cdot}94.$$

1·94 = percentage of manganese in the sample, as shown by colour test.

ESTIMATION OF SULPHUR IN PIG IRON.

Evolution and Gravimetric Method.

In ordinary pig iron, sulphur is estimated in the manner described for steels in previous pages.

Usually 5 grammes of the sample are taken, and a duplicate estimation is made on 4 or on 6 grammes.

But certain pig irons (notably white irons) do not yield all their sulphur by evolution when dissolved in hot hydrochloric acid. In such cases, M'Farlane & Gregory, of Frodingham,* adopt the following method:—

Weigh off 5 grammes of the sample.

Intimately mix the weighed portion with half a gramme of sulphur-free cream of tartar (potassium-hydrogen-tartrate, $C_4H_5KO_6$).

Wrap the mixture in filter-paper, and place in a crucible, cover the crucible, and place the whole in a muffle which is at a good red heat.

Allow to remain for about fifteen minutes, the muffle being kept at a red heat all the time.

Withdraw the crucible and contents, and, when cool, pound the mixture in a mortar, transfer to a 500 c.c. (about 17 ozs.) conical flask, and proceed with the estimation as detailed on pp. 43 to 54.

When there is occasion to suppose that all the

* See *Chemical News*, vol. xciii., p. 201.

sulphur has been evolved, take away the tube or flask through which the gases have been passed, and put another tube or flask with copper sulphate or cadmium sulphate solution in position, and continue the boiling for a few minutes. If a precipitate is formed, add it to that previously obtained. After experience has been gained, this precaution may be unnecessary.

Estimation of Sulphur in Pig Iron.

Gravimetric Method.

Outline of the Process.—A weighed quantity of the sample is treated with acids and with chlorate to dissolve the iron, &c., and to oxidise the sulphur and the silicon. The solution is evaporated to dryness; and more acid is added and evaporated. The dried mass is then boiled in acid, and the insoluble portion is separated by filtration. Barium chloride is added to the clear, hot filtrate. This causes the precipitation of barium sulphate—a reaction indicated by the equation,

$$K_2SO_4 + BaCl_2 = BaSO_4 + 2KCl.$$

Barium sulphate is insoluble in the acid solution. It is collected on a filter, washed, dried, ignited, cooled, and weighed. The percentage of sulphur is then calculated.

Details of the Process.—Weigh off 5 grammes of the sample.

Transfer the weighed portion to a 13 × 10·5 cm. (about 5 × 4 inches) Bohemian or Jena beaker.

Add 40 c.c. of pure 1·16 specific gravity hydrochloric acid along with 20 c.c. of pure 1·42 specific gravity nitric acid, and heat gently.

When brisk action has ceased, add a few crystals of potassium chlorate, or the chlorate crystals may be previously dissolved in one of the acids.

Evaporate to dryness on a hot plate (see note on hot plate, p. 149), and allow to bake for twenty minutes after.

Withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 25 c.c. of pure 1·16 specific gravity hydrochloric acid, and again evaporate to dryness on the hot plate.

Again withdraw the beaker and place it on a cork mat.

When the beaker is not likely to crack in contact with liquid, add 40 c.c. of pure 1·16 specific gravity hydrochloric acid.

Boil, to dissolve the iron, &c.

Evaporate till a skin begins to form.

Withdraw the beaker and allow it to cool a little.

Add 5 c.c. of pure hydrochloric acid and about 20 c.c. of warm water.

Stir the solution well and immediately decant it into a 12·5 cm. Swedish filter, collecting the filtrate (and washings) in a 13 × 10·5 cm. (about 5 × 4 inches) Bohemian or Jena beaker.

Rinse the beaker twice with a little hot water

Decant the liquid into the filter.

Allow the whole to drain into the beaker.

Wash the filter twice with water, and allow the washings to drain into the beaker. The solution and washings should not measure more than 75 c.c.

Remove the beaker and set it on the hot plate.

When the liquid boils, add, drop by drop, 6 c.c. of a 10 per cent. solution of barium chloride.

Place a clock-glass over the beaker and boil the contents briskly for a few minutes.

Place the beaker in a warm place to allow the precipitate to settle.

Decant the liquid into a 12·5 cm. Swedish filter, collecting the filtrate and washings in a clean beaker of suitable size.

Pour about 100 c.c. of hot water and 2 c.c. of hydrochloric acid into the beaker, and shake it so as to mix the liquid and the precipitate.

Allow to settle in a warm place.

Again decant into the filter.

Pour another 100 c.c. of water into the beaker, and shake it so as to mix as before.

Drain the liquid and precipitate into the filter.

Wash several times with water.

Test the last washings with acidulated silver nitrate solution (see p. 170).

Wash twice with water after all chlorides appear to have been washed out.

Place the funnel, with filter-paper and contents, on a filter dryer (Fig. 4, p. 14) on a hot plate, and allow to remain till dried.

Place the dried residue and filter-paper in a tared platinum or porcelain crucible or capsule.

Ignite in a hot muffle.

Withdraw the crucible, or capsule, and contents and place in a desiccator to cool.

Weigh, deduct the weight of the filter ash and the weight of barium sulphate in the blank, and calculate the percentage.

The weight of barium sulphate due to impurity in the acids used should be ascertained by a blank estimation, and deducted.

The blank estimation may be made on a mixture of 110 c.c of the hydrochloric acid and 20 c.c. of the nitric acid. These should be evaporated to small bulk, cautiously diluted with water, boiled, barium chloride solution added, and set aside for twelve hours at least to complete precipitation. The precipitate is collected on a filter, washed, dried, ignited, and weighed. The Winchesters containing the acids should be labelled, and set aside for sulphur estimations only.

It is assumed that the water used does not contain sulphates. If this is not so, a measured quantity of the water, equal to the quantity used for an ordinary estimation, must be included in the blank estimation.

As the amount of the precipitated sulphate in the acids and chlorate is usually very small, precipitation takes place very slowly. To ascertain more quickly, and probably more accurately, the weight of the sulphate due to these, two weighed quantities of a sample of pig iron may be treated with like

quantities of the acids and chlorate, and the barium sulphate estimated by the method detailed above.

An example may make this point more clear:—

Let "blank" represent the $BaSO_4$ from the acids and chlorate used.

Weight of $BaSO_4$ from $7\frac{1}{2}$ grammes
+ blank . . . . = 0·0475 gramme.
Weight of $BaSO_4$ from $2\frac{1}{2}$ grammes
+ blank . . . . = 0·0225 „

0·0250 „

The blank is the same in both cases, since equal quantities of acid and chlorate are used for each. The difference (0·025 gramme), therefore, shows the weight of $BaSO_4$ from 5 grammes of the sample.

$BaSO_4$ from 5 grammes . . = 0·0250 gramme.
„ $7\frac{1}{2}$ „ $= 0{\cdot}025 \times \frac{3}{2}$ = 0·0375 „

$BaSO_4$ from $7\frac{1}{2}$ grammes + blank = 0·0475 gramme.
„ $7\frac{1}{2}$ „ . . = 0·0375 „

$\therefore$ „ blank . . . = 0·0100 „

$BaSO_4$ from 5 grammes . . = 0·0250 gramme.
„ $2\frac{1}{2}$ „ $= 0{\cdot}025 \times \frac{1}{2}$ = 0·0125 „

$BaSO_4$ from $2\frac{1}{2}$ grammes + blank = 0·0225 gramme.
„ $2\frac{1}{2}$ „ . . = 0·0125 „

$\therefore$ „ blank . . . = 0·0100 „

Pure $BaSO_4$ contains 13·73 per cent. of sulphur, and, when 5 grammes are taken for analysis, the factor for ascertaining the percentage is

$$\frac{13{\cdot}73}{5} = 2{\cdot}746.$$

$$\text{Log } 2{\cdot}746 = 0{\cdot}4387005.$$

EXAMPLE—

Weight of crucible + ash and blank + precipitate	=	17·4607	grammes.
„ crucible . . .	=	17·4428	„
„ ash + precipitate .	=	0·0179	„
„ filter ash + blank .	=	0·0013	„
„ precipitate ($BaSO_4$)	=	0·0166	„

$$0{\cdot}0166 \times 2{\cdot}746 = 0{\cdot}046.$$

0·046 = percentage of sulphur in the sample of pig iron.

ANALYSIS OF LIMESTONE.*

The volatile matter is estimated by carefully driving off all that is volatile at a steady red heat, and another sample is treated for general analysis. With one exception—magnesia—the weighed precipitates are of the same composition as the components of the limestone.

The following analysis may be made on a sample which has been finely pounded and dried. Drying, however, is not always necessary—indeed, it is unusual in iron and steel works. But, in the event of a consignment of limestone being very wet, an estimation of the moisture may be made by the method detailed on pp. 254 and 255.

Estimation of Volatile Matter.

Outline of the Process.—A portion of the sample is weighed into a tared basin, and heated at a steady red heat until all the volatile matter is driven off. After allowing to cool, the basin (with its contents) is re-weighed. The percentage loss is then calculated.

* For analysis of calcined limestone, see p. 309.

Details of the Process.—Tare a 7·6 c.m. (about 3 inches) diameter platinum or porcelain basin, and note the weight.

Weigh into it 0·8 gramme of the finely-powdered sample.

Heat gently near the front of a muffle, taking care not to permit the carrying off of solid particles.

Heat more strongly by pushing the basin and contents to the hottest part of the muffle, and allowing to remain for about an hour. By this treatment the "volatile matter" is driven off.

Withdraw the basin to the slab in front of the muffle, and, when just cool enough to permit removal by hand, place it, with its contents, in a desiccator.

When cold, weigh and calculate.

EXAMPLE—

	Grammes.
Weight of basin	= 18·3775
„ sample	= 0·8000
„ basin and sample before ignition	= 19·1775
„ „ „ after ignition	= 18·8318
Loss of weight = volatile matter . .	= 0·3457

Then, as 0·8 gramme was taken for the estimation, the loss of weight $\times \frac{100}{8}$ = percentage of volatile matter.

$$\frac{0{\cdot}3457 \times 100}{0{\cdot}8} = 0{\cdot}3457 \times 125 = 43{\cdot}21 = \text{per cent.}$$

of the volatile matter in the sample of limestone.

To make sure that all volatile matter has been driven off, the basin and contents may be reheated in the hottest part of the muffle for an hour, and, after cooling in the desiccator, re-weighed.

The chief constituent of the "volatile matter" is carbon dioxide. Its percentage may be inferred from the result obtained by the following method:—

Weigh into a tared basin 5 grammes of the pounded sample.

Keep the basin and contents in a steam oven at 100° C. for about two hours.

Allow to cool in a desiccator.

The loss of weight = the water driven off; the remainder of the volatile matter may be accepted as carbon dioxide. Occasionally a little organic matter is present.

EXAMPLE—

	Grammes.
Water driven off . . .	= 0·024

$$0{\cdot}024 \times \frac{100}{5} = 0{\cdot}48,$$

and 0·48 = percentage of moisture.

Percentage of volatile matter, .	43·21
„ water, . . .	0·48
„ carbon dioxide, .	42·73

When required, the percentage of carbon dioxide may be ascertained by means of a Schroedter's apparatus.

Estimation of Insoluble Matter.

Outline of the Process.—The weighed portion of the sample is boiled in hydrochloric acid solution, water is added, and the insoluble matter is collected on a filter, washed, dried, ignited, and weighed. From the ascertained weight the percentage is calculated.

Details of the Process.—Weigh off 1 gramme of the finely-pounded sample.

Transfer the weighed portion to a 400 c.c. beaker.

Add about 20 c.c. of warm water, and shake the beaker so as to mix the sample well with the water.

Add 10 c.c. of 1·16 specific gravity hydrochloric acid. If the limestone contains more than traces of iron, about 5 c.c. of nitric acid should also be added to facilitate separation at a subsequent stage.

Set the beaker and contents on a hot plate, and heat to boiling point.

Add about 30 c.c. of hot water.

Boil briskly.

Wash the insoluble residue into a 9 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash thoroughly with dilute hydrochloric acid—say 1 of 1·16 specific gravity acid to 10 of water—and afterwards with hot water.

Dry the residue and filter-paper.

Put the filter-paper and the residue in a tared platinum or porcelain capsule, and place in a hot muffle.

Allow to remain for half an hour.

Withdraw, and, when cool enough to just permit removal by hand, place the capsule and contents in a desiccator.

When cold, weigh.

EXAMPLE—

		Grammes.
Weight of capsule + ash + precipitate .	=	17·3983
„ capsule	=	17·3863
„ ash and precipitate . .	=	0·0070
„ filter ash	=	0·0007
„ residue	=	0·0063

Then, as 1 gramme was taken for the estimation, the weight of residue $\times \frac{100}{1} =$ percentage of residue.

$0{\cdot}0063 \times 100 = 0{\cdot}63 =$ percentage of insoluble residue in the sample of limestone.

The insoluble residue, as a rule, consists largely, if not entirely, of silica. If the percentage of silica is required, it should be estimated after fusion.

Estimation of Alumina.

Outline of the Process.—The filtrate from the separation of the insoluble matter is heated to boiling point, and a slight excess of ammonia liquor is added to precipitate the alumina and any ferric oxide present. Some of the excess ammonia is boiled off, the solution being left faintly alkaline. The precipitate is collected, washed, dried, ignited, and weighed. The percentage is then calculated.

Details of the Process.—To the filtrate from the insoluble matter, add 2 or 3 c.c. of 1·42 specific gravity nitric acid.

Boil.

Add a slight excess of ammonia liquor. This will cause the separation of a gelatinous precipitate of aluminium hydrate. If pure, the precipitate will be white, but if iron is present it will also be precipitated —as reddish-brown ferric hydrate.

Boil until faintly alkaline.

Immediately wash the precipitate on to a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 700 c.c. beaker.

Wash several times with hot water.

Dry the precipitate and filter-paper.

Put the precipitate and filter-paper in a tared platinum or porcelain capsule, and place near the front of a muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for about thirty minutes.

Withdraw the capsule, and, when just cool enough to permit removal by hand, place it in a desiccator.

When cold, weigh.

EXAMPLE—

		Grammes.
Weight of	capsule + ash + precipitate	= 17·3922
„	capsule	= 17·3863
„	ash + precipitate . .	= 0·0059
,	filter ash	= 0·0008
„	precipitate (Al_2O_3) . .	= 0·0051

Then, as 1 gramme was taken for the estimation, the weight of $Al_2O_3 \times \frac{100}{1}$ = percentage of Al_2O_3.

$0·0051 \times 100 = 0·51$ = percentage of alumina in the sample of limestone.

When iron is present in appreciable amount an estimation may be made on a separate portion of the sample. The corresponding weight of ferric oxide should then be calculated and deducted from the total weight of the precipitate, the difference being taken as alumina.

Weight of Fe × 1·429 = weight of Fe_2O_3.

Estimation of Lime.

Outline of the Process.—The filtrate from the separation of the alumina is heated nearly to the boiling point. Ammonia liquor and ammonium chloride are added. A hot solution of ammonium oxalate is then added to precipitate the lime as calcium oxalate. The precipitate is collected on a filter, washed, ignited, and the resulting calcium oxide is weighed. The percentage is then calculated.

Details of the Process.—Heat the filtrate from the separation of alumina to the boiling point.

If there is reason to believe that the sample contains much magnesia, add 10 c.c. of a strong solution of ammonium chloride. This prevents the precipitation of magnesia when ammonium oxalate is added, and checks the solvent action of magnesium chloride on calcium oxalate.

Add about 10 c.c. of 0·88 specific gravity ammonia liquor.

Add 40 c.c. of hot ammonium oxalate [$C_2(NH_4)_2O_4$] solution (see p. 163). This will cause the precipitation of calcium oxalate (C_2CaO_4). The reaction is:—

$$CaCl_2 + C_2(NH_4)_2O_4 = C_2CaO_4 + 2(NH_4)Cl.$$

Continue the boiling for about one minute.

Set the beaker in a warm place to allow the precipitate to subside.

Wash the precipitate on to a 12·5 cm. Swedish filter, collecting the filtrate and washings in a 1,000 c.c beaker.

Wash thoroughly with hot water.

Dry the precipitate.

Place the dried precipitate and filter-paper in a tared platinum or porcelain capsule near the front of the muffle.

After about ten minutes, remove the capsule to the hottest part of the muffle, and allow to remain there for forty minutes at least. This will cause the decomposition of the calcium oxalate: carbon monoxide and carbon dioxide will be evolved, while calcium oxide (lime) will remain.

The reaction is:—

$$CaC_2O_4 = CaO + CO_2 + CO.$$

Withdraw the capsule, and, when it is just cool enough to be lifted by the hand, place it with its contents in a desiccator.

When cold, weigh.

EXAMPLE—

	Grammes.
Weight of capsule + ash + precipitate	= 18·9327
„ capsule	= 18·3773
„ ash and precipitate . .	= 0·5554
„ filter ash	= 0·0008
„ precipitate (CaO) . .	= 0·5546

Then, as 1 gramme was taken for the estimation, the weight of CaO $\times \frac{100}{1}$ = percentage of CaO.

$0·5546 \times 100 = 55·46$ = percentage of CaO in the sample of limestone.

Estimation of Magnesia.

Outline of the Process.—The filtrate from the separation of the lime is heated to about 60° C., and ammonium phosphate solution is added to precipitate the magnesia as ammonium-magnesium-phosphate. This is collected on a filter, washed, dried, carefully ignited, and weighed. From the weight of the resulting magnesium pyrophosphate the percentage is calculated.

Details of the Process.—To the still warm filtrate from the lime estimation add one-tenth bulk of ammonia liquor (sp. gr. 0·88).

Add about 5 c.c. of 20 per cent. ammonium phosphate [$(NH_4)_2HPO_4$] solution (see p. 164). If the sample contained magnesia, a white precipitate of ammonium-magnesium-phosphate [$Mg(NH_4)PO_4 . 6H_2O$] will be formed, the reaction being—

$$MgCl_2 + NH_3 + (NH_4)_2HPO_4 + 6H_2O = Mg(NH_4)PO_4 . 6H_2O + 2(NH_4)Cl.$$

Stir briskly, and allow the precipitate to settle.

Filter through a 12·5 cm. Swedish filter.

Wash about eight times with ammonia water (1 of ammonia liquor (sp. gr. 0·88) to 8 of water),

Test the last washings with acidulated silver nitrate (see p. 170).

Wash two or three times with the ammonia water after all the chlorides have apparently been washed out.

Dry the precipitate and filter.

Ignite, cool, and weigh.

The filter should be thoroughly dried, and the ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes impossible to burn off the paper. During ignition, the precipitate loses water and is converted into magnesium pyrophosphate ($Mg_2P_2O_7$), thus

$$2Mg(NH_4)PO_4 . 6H_2O = Mg_2P_2O_7 + 2NH_3 + 7H_2O.$$

EXAMPLE—

		Grammes.
Weight of	capsule + ash + precipitate	= 17·3946
„	capsule	= 17·3862
„	ash and precipitate . .	= 0·0084
„	filter ash	= 0·0008
„	precipitate ($Mg_2P_2O_7$) .	= 0·0076

Magnesium pyrophosphate contains 36·243 per cent. of magnesia (MgO).

Log 36·243 = 1·5592241.

Then, as 1 gramme was taken for the estimation, the weight of $Mg_2P_2O_7$ × 36·243 = percentage of MgO.

0·0076 × 36·243 = 0·275 ≒ 0·28 = percentage of magnesia in the sample of limestone.

SUMMARY OF RESULTS.—Raw limestone.

	Per cent.
Volatile matter, . . .	43·21
Silica, ...	0·63
Alumina, ...	0·51
Lime, ...	55·46
Magnesia, ...	0·28
Sulphur, &c. (not estimated), .	...
	100·09

ANALYSIS OF CALCINED LIMESTONE.

Proceed as in the analysis of limestone, but for the estimation of volatile matter use 10 grammes of the sample. For precipitating the lime, use 60 c.c. of ammonium oxalate solution (see p. 163), and for precipitating the magnesia use 4 c.c. of 20 per cent. ammonium phosphate solution.

ANALYSIS OF DOLOMITE.

Outline of the Process.—With the exception of the modifications required on account of the higher percentage of magnesia in dolomite, the method of analysis is the same as detailed for limestone in the preceding pages.

Estimation of Volatile Matter.—Proceed as directed for limestone on pp. 98 to 100, but, as the volatile matter is sometimes more difficult to drive off, continue the heating for a longer period.

Estimation of Insoluble Matter.—Proceed as directed for limestone on pp. 101 and 102.

Estimation of Alumina and Oxide of Iron.—Proceed exactly as directed on pp. 103 and 104.

Estimation of Lime.—Proceed as directed on pp. 105 and 106, except that, before precipitating the lime, add a strong solution of about 6 grammes of ammonium chloride. This prevents the precipitation of magnesia when oxalate is added, and, further, it checks the solvent action of magnesium chloride on calcium oxalate.

Estimation of Magnesia.—Proceed as directed for limestone estimation, but use 15 c.c. of the 20 per cent. ammonium phosphate solution (see p. 164).

PROXIMATE ANALYSIS OF SOLID FUELS—COAL, COKE, &c.

Particular attention should be paid to the mechanical condition of the fuel. For the estimation of ash and of moisture the sample operated on should be very finely powdered. If the sample supplied is not finely powdered, a portion of the sample should be carefully selected, and the whole of the selected portion crushed fine enough. From the finely powdered sample the necessary quantities should be accurately weighed off.

The estimations required are—

(*a*) Estimation of moisture.
(*b*) Estimation of ash.
(*c*) Estimation of coke.
(*d*) Calculations of the percentage of fixed carbon ; and also
(*e*) An abstract of results.

(*a*) Estimation of Moisture.

Select a flat porcelain basin of about 7 cm. (or $2\frac{3}{4}$ inches) diameter, wipe it dry, weigh, and note the weight.

The basin may be dried by heating it over the flame of a Bunsen burner (care being taken not to crack the basin) for 5 or 10 minutes, and allowing it to cool in a desiccator.

Weigh into the basin 2 grammes of the finely powdered sample.

Set the basin and contents in a steam oven at

about 100° C., and allow to remain there for 1½ hours.*

Take the basin and contents from the steam bath, and allow to cool in a charged desiccator. (Continue to keep the steam bath up to 100° C.)

When cool, weigh, and note the weight.

Set the basin and contents back in the hot steam oven ; allow to remain for about 15 minutes or more, withdraw, and replace in the desiccator, and, when cool, reweigh and note the weight found.

If necessary, repeat the heating, cooling and weighing.

EXAMPLE—

Before drying—	Grammes.
Weight of basin + sample	= 19·4375
Weight of basin only	= 17·4375
Weight of sample	= 2·0000
Weight of basin + sample before drying	= 19·4375
Weight of basin + sample after drying	= 19·3533
	0·0842

$$\frac{0{\cdot}0842 \times 100}{2} = 0{\cdot}0842 \times 50 = 4{\cdot}21.$$

4·21 = percentage of moisture in the sample.

NOTE.—Time permitting, the dried sample may be used for the estimation of ash, by

* Some, if not all, samples of coal when heated too long gain in weight, owing, it is supposed, to the oxidation of sulphur in the sample. The writer found that the maximum loss of weight from a large number of coals was obtained on heating for 1¾ hours.

cautiously burning off all combustible matter (in a muffle), allowing to cool in a desiccator, weighing and calculating.

(*b*) Estimation of Ash.

Either use the dried sample—from the estimation of moisture—or

Select a round bottomed porcelain basin about 7 cm. (or $2\frac{3}{4}$ inches) diameter, wipe it dry, weigh and note the weight.

Weigh into the basin 2 grammes of the finely pounded sample.

Place the basin and sample in front of a hot muffle, and, after a little time, push the basin and contents further in, and, after a little more time, place them in the hottest part of the muffle.

Allow to remain until all the combustible components have burned off.

Withdraw the basin to the sole in front of the muffle.

When partly cooled place in a charged desiccator, and, when fully cooled, weigh.

Example—

	Grammes.
Weight of basin + ash	= 17·5622
Weight of basin only	= 17·4375
	0·1247

$$\frac{0{\cdot}1247 \times 100}{2} = 0{\cdot}1247 \times 50 = 6{\cdot}235.$$

6·24 $\doteqdot$ percentage of ash in the sample.

(*c*) Estimation of Coke obtainable from Coal.

Dry a No. 2 porcelain crucible and lid.

Weigh the crucible and lid, and note the weight.

Weigh into the crucible 10 grammes of the powdered sample, taking care to see that the lid is kept on the balance pan while weighing off the sample.

Place the lid on the crucible.

Place the whole in a warm part of a hot muffle.

In a short time a flame should appear between the crucible and the rim of the lid.

Keep the crucible, with the lid on, in the muffle as long as the flame can be seen.

Withdraw the crucible, &c., to the sole in front of the muffle.

Allow to remain there until partly cooled.

Place in a charged desiccator, and, when fully cooled, weigh.

Example—

Before coking—	Grammes.
Weight of crucible and lid + sample	= 40·5362
Weight of crucible and lid	= 30·5362
Weight of sample taken	= 10·0000
After coking—	
Weight of crucible + lid + coke	= 37·2713
Weight of crucible and lid only	= 30·5362
	6·7351

$$\frac{6{\cdot}7351 \times 100}{10} = 6{\cdot}7351 \times 10 = 67{\cdot}35.$$

67·35 = percentage of coke.

(*d*) Calculation of Percentage of Fixed Carbon.

	Grammes.
Percentage of coke as found by experiment	= 67·351
Percentage of ash as found by experiment	= 6·235
	61·116

61·116 = percentage of fixed carbon.

(*e*) Abstract of Results.

	Grammes.
Fixed carbons	= 61·12
Volatile carbon (hydrocarbons, &c.) *	= 28·43
Ash	= 6·24
Moisture	= 4·21
Total	= 100·00

ESTIMATION OF SULPHUR IN COAL OR COKE.

Weigh off 9 grammes of partly slaked lime which is as free as possible from sulphur and silica. (The amount of sulphur in the lime must be esti mated and deducted.)

Place about half of it in a 7 cm. (about $2\frac{3}{4}$ inches) round bottomed porcelain basin.

Weigh off (accurately) 3 grammes of the carefully selected and finely-powdered sample of coal or coke.

Transfer the weighed sample to the basin.

* By difference.

Stir so as to mix the lime and the weighed sample thoroughly.

Spread the remainder of the weighed lime over the mixture, so as to form a covering.

Place the basin and contents in a hot muffle.

Allow to remain for at least 45 minutes.

Draw the basin to the front of the muffle, and stir up the contents so as to expose any unburnt portions.

Replace in hot part of the muffle.

Allow to remain for 10 minutes or more.

Stir up the contents again, and search for unburnt coal or coke.

If the carbon has all been burned off, place the basin in a safe place to cool a little.

Transfer the contents to a 13·5 × 8 cm. (about $5\frac{1}{2}$ inches × $3\frac{1}{4}$ inches) beaker.

Add about 50 c.c. of water.

Add about 2 c.c. of bromine and stir well.

Add a sufficient quantity of strong hydrochloric acid to dissolve the lime, &c.—about 33 c.c. should be sufficient.

Boil briskly for at least five minutes.

Filter, collecting the filtrate (and washings) in a clean 6-inch × $3\frac{3}{4}$-inch beaker.

Wash well with hot water.

Heat the filtrate and washings just to boiling point.

Add 10 c.c. of warm 10 per cent. barium chloride solution.*

* The barium chloride presented is capable of precipitating 0·131 gramme of sulphur = 0·952 gramme of $BaSO_4$ = 4·57 per cent. of sulphur from the coal or coke : a plentiful excess.

Place a clock glass on the beaker.

Boil briskly for about seven minutes

Allow the precipitate to settle.

Wash three times by decantation through a 9 cm. Swedish filter.

Wash the precipitate on to the filter.

Wash about ten times with hot water.

Test the washings for the presence of chlorine.

If necessary, continue the washing.

Dry the filter paper and precipitate.

Ignite in a tared No. 0 porcelain crucible for about thirty minutes in a hot muffle.

Allow to cool in a desiccator.

Weigh, and calculate the result.

EXAMPLE—

	Grammes.
Weight of crucible + precipitate + ash	= 7·1343
Weight of crucible	= 7·1263
Weight of precipitate + ash	= 0·1911
Weight of ash + $BaSO_4$ due to sulphur in the lime used	= 0·0041
Weight of $BaSO_4$ due to sulphur in the sample	= 0·1870

$$\frac{0{\cdot}187 \times 32 \times 100}{233 \times 3} = 0{\cdot}187 \times 4{\cdot}587 = 0{\cdot}856.$$

0·856 = percentage of sulphur in the sample.

ESTIMATION OF IRON.

Volumetric Methods.

Frequently the amount of iron in a substance may be conveniently and accurately ascertained by a volumetric method. For this purpose the sample must be brought into solution under proper conditions. Standard solution of an oxidising agent is then added from a measuring apparatus, and, when the oxidation is complete, the measured volume of the standard solution is noted and the necessary calculations are made.

Towards the end of a reaction the standard solution is cautiously added drop by drop, and as the strength or power of the standard solutions are known, such volumetric estimations are known as titrations—from a French word, *titre*, signifying power or capacity.

The methods generally employed in the volumetric estimation of iron are :—

(*a*) Marguerite's—the Permanganate method—
and
(*b*) Penny's—the Dichrome method.

Both methods are based on the amount of oxidising agent required to convert ferrous salt to ferric salt.

The dichrome method is generally preferred in British iron works.

In each case a weighed portion of the sample is dissolved in acid. If all the iron is not in the ferrous state it must be reduced—unless it is intended to estimate, separately, the ferrous and ferric iron—and any excess of reducing agent driven off or "corrected." The solution (reduced if necessary) is subjected to the selective, oxidising action of a standardised solution carefully measured from a burette. When the ferrous iron has all been oxidised, the quantity of standard solution used is read off and the necessary calculations made.

The state in which the iron exists in a solution is shown by **indicators**, thus—

A drop of acidified ferrous solution, when brought into contact with a drop of weak solution of ferricyanide (not ferrocyanide) of potash, yields a blue colouration or a blue precipitate.

A drop of acidified ferric solution, when brought into contact with a drop of alkaline sulpho-cyanide (thiocyanate of ammonia, potash, or soda) solution, shows a blood-red colour, or, if in very small quantity, a faint pink colour.

Convenient reducing agents are nascent hydrogen (from action of acid on zinc); sulphurous anhydride; and, for dichrome titration, stannous chloride.

Estimation of Iron by Titrating with a Standard Solution of Potassium Permanganate ($K_2O \cdot Mn_2O_7$).

The reaction which takes place on peroxidising ferrous iron may be represented thus:—

$$K_2O \cdot Mn_2O_7 + 10FeO, SO_3 + 8H_2SO_4 = 5Fe_2O_3, 3SO_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

When all the iron has been oxidised to the ferric state further additions of potassium permanganate impart a pink colour to the liquid in the flask.

Quantity of potassium permanganate required for standard solution for the estimation of iron.

The molecular weight of potassium permanganate is 316·3.

316·3 grammes can peroxidise 55·9 × 10 grammes of ferrous iron, and

$$\frac{316{\cdot}3}{559} = 0{\cdot}56533.$$

or every gramme of iron requires 0·56583 gramme of permanganate.

If, therefore, 5·6583 grammes of potassium permanganate are dissolved and made up with water (at 15·5° C.) to 1 litre, every c.c. of the solution will equal 0·01 gramme of iron.

Preparation of Standard Solution of Permanganate for the Estimation of Iron.

Pound in a mortar about 2 grammes of pure potassium permanganate. This will be a sufficient quantity for a student to experiment on.

Dry the pounded sample.

Weigh off 1·415 gramme of the salt. (The theoretical quantity required is 1·4146 gramme.)

Transfer the weighed quantity to a 400 c.c. beaker or beaker flask.

Add about 100 c.c. of warm distilled water.

With a glass rod (without rubber) stir well to hasten solution.

Pour some of the liquid into a 250 c.c. glass-stoppered graduated flask, taking care not to allow any undissolved salt to enter the flask.

Add more warm distilled water to the contents of the beaker.

Stir well, as before.

Pour off more of the solution into the flask.

Make sure that all the salt is dissolved.

Transfer the remainder of the solution to the graduated flask.

Make up nearly to the mark with cold water.

Bring the solution to 15·5° C. and make up to the mark with water at that temperature.

Stopper the flask and shake it briskly.

NOTE.—Once a standard solution is made up it must be kept carefully stoppered. If a quantity of standard

solution is made for stock, the containing bottle should have a label showing the strength of the solution and the date of standardising. Portions of the standard solution which have been taken out must not be returned to the bottle.

Preparation of a Sample of Mohr's Salt for Standardising.

Mohr's salt is a compound sulphate of iron and ammonium $Fe(NH_4)_2(SO_4)_2 . 6H_2O$ and, when pure, contains 14·26 per cent., or nearly one-seventh its weight of ferrous iron. It may be purchased "chemically pure," or be prepared in the laboratory by the following method:—

Weigh off 27·8 grammes of pure recrystallised ferrous sulphate ($FeSO_4 . 7H_2O$).

Dissolve in minimum quantity of water at 40° C.

Weigh off 13·2 grammes of pure ammonium sulphate, $(NH_4)_2SO_4$.

Dissolve in minimum quantity of cold water.

Pour the ammonium sulphate solution into the solution of ferrous sulphate.

A granular precipitate of the double sulphate forms as the solution cools.

Wash by decantation.

Dry between the folds of bibulous paper under a press.

Preserve the dried sample in a clean, dry, stoppered bottle.

Articles Required for Standardising the Permanganate Solution.

These articles should all be ready before beginning to standardise.

A 30 or 50 c.c. burette, graduated in one-tenths; burettes for permanganate solution must have glass stopcocks.

An Erdmann's float.

A burette stand.

Three clean, dry, 10-oz. conical or globular flasks.

The standard solution, and

About 10 grammes of pure, dry Mohr's salt or a few grammes of pure iron wire.

Standardising the Permanganate Solution by Mohr's Salt.

Clean the burette, first with water and then with some of the standard permanganate solution.

Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with standard permanganate solution.

Put in the Erdmann's float and adjust to zero.

Weigh off accurately about 1·75 grammes of the Mohr's salt, and note the weight taken.

Transfer to a clean, dry 300 c.c. (about 10-oz.) conical or globular flask.

Add 100 c.c. of distilled water, to which about

5 c.c. of pure sulphuric acid has previously been added.

Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile or piece of white paper when examining for the colour.

Continue to add standard permanganate solution cautiously, and with occasional shaking of the flask, until a faint permanent pink colour appears.

The reaction may be expressed by the equation—

$$K_2O \cdot Mn_2O_7 + 10FeO, SO_3 + 8H_2SO_4 = 5Fe_2O_3, 3SO_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Read off and note the quantity of standard permanganate solution required to complete the reaction.

A little quantity of the permanganate solution is required to impart a pink tint to the solution in which the salt was dissolved To allow for this a **blank experiment** should be made thus:—

Into a 300 c.c. (about 10-oz.) conical flask measure 100 c.c. of distilled water and 6 c.c. of pure sulphuric acid.

Note the amount of standard solution in the burette, and from it run two or three drops into the conical flask.

Shake the flask so as to mix the contents.

Compare the pink tint with that in the flask in which the iron estimation has just been made.

If necessary, add more standard permanganate to bring the liquid to the same depth of colour.

Note the quantity taken, and deduct from the amount noted as required to effect the oxidation of the iron solution.

Calculate the result.

EXAMPLE OF CALCULATION—

1·776 gramme of Mohr's salt required 25·30 c.c. of the standard permanganate solution, after making allowance for the blank colouration.

$$\text{Iron in Mohr's salt, } \frac{1{\cdot}776 \times 14{\cdot}26}{100} = 0{\cdot}2533,$$

$$\frac{0{\cdot}2533}{25{\cdot}30} = 0{\cdot}010012.$$

Every 1 c.c. of the standard permanganate solution = 0·010012 gramme of iron.

Experiments on 2·035 grammes and on 1·638 grammes, together with the result recorded above, showed that (on an average) every c.c. of the standard permanganate solution = 0·010011 gramme of iron.

EXERCISES IN THE ESTIMATION OF IRON BY MEANS OF STANDARD PERMANGANATE SOLUTION.

Clean a burette with distilled water and then with standard permanganate solution. Run off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution, put in an Erdmann's float, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a clean, dry 300 c.c. (about 10-oz) conical or globular flask.

Add about 100 c.c. of water to which about 5 c.c. of sulphuric acid has been added.

Shake the flask until the salt has dissolved.

Add standard permanganate solution from the burette to the solution in the flask as long as the colour readily disappears.

Set the flask on a white tile, or a piece of white paper, when examining for colour.

Continue to add the standard permanganate solution cautiously, and with occasional shaking, until a faint pink colour is obtained which is permanent even after shaking the flask.

Read off, and note the quantity of standard solution required to complete the reaction.

Deduct the quantity required for blank.

Calculate the result.

EXAMPLE—

Weight of Mohr's salt taken = 2·0092 grammes. Standard permanganate solution required, less the quantity for blank = 28·61 c.c.

Every c.c. = 0·010011 gramme of iron.

28·61 × 0·010011 = 0·2864 gramme.

0·2864 = weight of iron found in 2·0092 grammes of Mohr's salt.

$$\frac{0{\cdot}2864 \times 100}{2{\cdot}0092} = 14{\cdot}254$$

and 14·254 = percentage of iron found in Mohr's salt.

Having—by means of standard permanganate solution—oxidised the iron to the ferric state, the iron in the solution should now be *reduced* to the ferrous condition.

Reduction of ferric solutions may be effected by means of a reductor (see p. 160) or by adding granulated zinc, or small pieces of thin stick zinc and sulphuric acid. The zinc used for this purpose should be free from iron. The reaction between the zinc and acid gives rise to the evolution of hydrogen:—

H_2SO_4	+	Zn	=	$ZnSO_4$	+	2H
Sulphuric acid	and	zinc	yield	zinc sulphate	and	hydrogen.

The zinc sulphate remains in solution, and takes no part in the work; the ferric salts are reduced to ferrous by the action of nascent hydrogen, thus:—

$Fe_2(SO_4)_3$	+	2H	=	$2FeSO_4$	+	H_2SO_4
Ferric sulphate	and	hydrogen	yield	ferrous sulphate	and	sulphuric acid.

To ascertain if all the ferric iron has been reduced, bring a drop of the solution on the end of a stirring rod into contact with a drop of dilute thio-cyanate (sulphocyanide) solution on a white enamelled slab or a piece of drop-reaction paper. If more than a faint pink colour results, reduction is not complete.

Prof. M. M. Pattison Muir points out (*Chemical News*, 31st January, 1908) that if a small quantity of zinc is used for effecting reduction the action is slow, and if a large quantity of zinc is used time is lost in completing its solution. He suggests the addition of

saturated aqueous solution of mercuric chloride as soon as the reduction is finished. This stops the further action of acid on the remaining zinc, and allows the titration to be proceeded with at once. The author now uses mercuric sulphate in dilute sulphuric acid to stop the action of acid on the zinc. This he prefers to the usual practice of filtering through glass wool.

Sulphurous anhydride, as supplied in syphons, is very convenient for reducing ferric solutions. Water strongly charged with the gas is poured into the solution, and a reaction takes place which may be represented by the equation—

Fe_2O_3	+	H_2O	+	SO_2	=	$2FeO$	+	H_2SO_4
Ferric oxide	and	water	and	sulphurous anhydride	yield	ferrous oxide	and	sulphuric acid.

If sulphurous anhydride is used as the reducing agent, excess must be boiled off.

When the solution has been brought into proper condition, proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again, and repeat the titration.

Estimation of Iron in Ore by Means of Standard Permanganate Solution.

Before making an assay by titration, the student should practise the exercises set on the previous pages.

Collect the articles required (see p. 123).

Clean the burette, first with water, and then with some of the standard permanganate solution. Run

off, into a sink, the permanganate solution used for cleaning the burette.

Fix the burette in a stand.

Nearly fill the burette with standard permanganate solution. This solution should, after two or three weeks, be restandardised before using.

Place an Erdmann's float in the solution in the burette.

Adjust the float to zero.

The ore, having been carefully sampled, and the sample pounded, well mixed, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Place the weighed portion in a 300 c.c. (about 10 ozs) conical flask.

Add about 100 c.c. of dilute sulphuric acid (6 vols. of acid to 100 of water).

Put a funnel in the neck of the flask, and set on a hot plate so as to hasten solution.

When all the iron has dissolved, remove the flask, wash the condensed liquid on the funnel into the flask, and reduce the ferric oxide as directed on p. 127.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken, and deduct the blank.

Calculate the percentage (see example on p. 126).

If ferrous and ferric oxides are required, proceed as directed on p. 139.

Estimation of Iron by Titrating with a Standard Solution of Potassium Dichromate ($K_2Cr_2O_7$ or $K_2O \cdot 2CrO_3$).

This orange-coloured salt (commonly called "bichrome") can be readily obtained in a fair state of purity, and its solution, if properly kept, remains constant in strength for a long time: it is practically permanent. Under easily-established conditions it parts with oxygen to ferrous oxide (FeO), converting it into ferric oxide (Fe_2O_3).

By measuring the amount of standardised dichrome solution required to effect the change, the amount of iron which was present in the ferrous state can be ascertained.

The chemical changes which take place when iron is dissolved in hydrochloric acid may be expressed by the following equation:—

Fe	+	$2HCl$	=	$FeCl_2$*	+	H_2
Iron	and	hydrochloric acid	yield	ferrous chloride	and	hydrogen.

On adding dichrome solution the ferrous chloride is acted on, and the chemical reactions which occur may be indicated thus:—

$6FeCl_2$	+	$K_2Cr_2O_7$	+	$14HCl$		
Ferrous chloride	and	dichrome	and	hydrochloric acid		
=	$3Fe_2Cl_6$	+	Cr_2Cl_6	+	$2KCl$	+	$7H_2O$
yield	ferric chloride	and	chromic chloride	and	potassium chloride	and	water.

* Unless precautions are taken, the ferrous solution soon becomes more or less completely converted into ferric solution having a yellow colour.

This equation shows that 1 gramme of iron requires 0·878 gramme of dichrome to complete the reaction.

To Prepare a Standard Solution for the Estimation of Iron.

Weigh off 17·6 grammes of pure, dry dichrome. This quantity is, in practice, more convenient than the theoretical amount—17·56 grammes.

Transfer to a graduated litre flask.

Dissolve the salt in about 600 c.c. of distilled water, and, when the solution is at 15·5° C., make up to the mark with distilled water at that temperature.

Pour, if necessary through a dry filter, into a Winchester quart bottle.

Measure another litre of water in the graduated flask, and pour or filter it into the Winchester.

Mix the solution thoroughly.

To Standardise the Dichrome Solution.

Collect the following solutions and articles on the working bench :—

The prepared dichrome solution.

A dilute solution of stannous chloride (see p. 171) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferricyanide. This must not be confounded with

the more common ferrocyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs about 10 c.m. (or 4 inches) square.

Stirring rods for the ferricyanide and the thiocyanate solutions.

A porcelain basin about 7 inches diameter.

A glass rod about 8 inches long.

A reagent bottle containing pure re-distilled hydrochloric acid.

A wash-bottle containing hot water.

A burette stand, and

A burette, graduated in one-tenths.

Iron wire, pure by preference, or pure, dry ferrous ammonium sulphate or Mohr's salt (see composition on p. 122).

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the dichrome solution, and adjust to zero.

Clean the porcelain slab, and wipe it with a piece of clean filter-paper.

Weigh off accurately about 2 grammes of Mohr's salt, note the weight taken, and transfer to the porcelain basin.

Add about 150 c.c. of distilled water, and about 50 c.c. of hot water.

Add about 20 c.c. of pure re-distilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of dichrome solution required to complete the reaction.

Calculate as in the following example:—

2·0336 grammes of Mohr's salt, which contains 14·26 per cent. of iron, required 28·85 c.c. of the dichrome solution.

Iron in weighed quantity of Mohr's salt

$$= \frac{2{\cdot}0336 \times 14{\cdot}26}{100} = 0{\cdot}28999 \text{ gramme.}$$

Value of the dichrome solution

$$\frac{0{\cdot}28999}{28{\cdot}85} = 0{\cdot}01005.$$

∴ Every 1 c.c. of the standard dichrome solution = 0·01005 gramme of iron.

Make one or two additional estimations, and if all nearly agree, the mean may be taken. The winchester may then be labelled so as to show the strength of the solution and the date of standardising.

Exercises in the Estimation of Iron by Means of Standard Dichrome Solution.

Collect the solutions and articles mentioned on pp. 131 and 132.

Clean the burette, first with water, and then with standard dichrome solution. Run off, into a sink, the dichrome solution used for cleaning the burette.

Fix the burette in the stand.

Nearly fill the burette with the standard solution, and adjust to zero.

Weigh off accurately about 2 grammes of pure, dry Mohr's salt, and note the weight taken.

Transfer the weighed quantity to a 7-inch porcelain basin.

Add about 150 c.c. of distilled water, 50 c.c. of hot water, and 20 c.c. of pure, redistilled hydrochloric acid.

Stir until the salt is dissolved.

Proceed to titrate by running in standard dichrome solution to oxidise the ferrous iron.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

Note the quantity of solution required to complete the reaction.

Calculate as shown in the example on p. 126.

Having, by means of the dichrome solution, oxidised the iron to the ferric state, the iron in the solution should now be reduced to the ferrous condition.

Solutions containing ferric iron are reduced by the addition of acid solution of stannous chloride ($SnCl_2$), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus:—

Fe_2Cl_6	+	$SnCl_2$	=	$SnCl_4$	+	$2FeCl_2$
Ferric chloride	and	stannous chloride	yield	stannic chloride	and	ferrous chloride.

To find the exact point at which the reduction to ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

To guard against presence of excess of stannous chloride (which excess would spoil the accuracy of the estimation), about 4 c.c. of a 5 per cent. solution of mercuric chloride is added to the iron solution which has just been reduced. Excess of stannous chloride, if present, forms a white precipitate when the mercuric chloride is added. The following equation represents the change:—

$SnCl_2$	+	$2HgCl_2$	=	Hg_2Cl_2	+	$SnCl_4$
Stannous chloride	and	mercuric chloride	yield	mercurous chloride	and	stannic chloride.

The ferrous solution will then be ready for re-titrating with standard dichrome solution.

Proceed with the titration as before. The result should correspond with the one previously obtained. If not, reduce again and repeat the titration.

A brief recapitulation may now be useful.

Ferric solutions are yellow-coloured; ferrous solutions are colourless.

Ferric solutions yield a blood-red colour when mixed with solution of ammonium thiocyanate (sulphocyanide); ferrous solutions do not.

Ferrous solutions form a blue precipitate or show a blue colour when mixed with potassium ferricyanide solution; ferric solutions do not.

Stannous chloride reduces ferric solutions to ferrous.

Mercuric chloride precipitates and corrects excess of stannous chloride.

Dichrome oxidises ferrous iron in solution to the ferric state, and is unaffected by presence of manganese or other salts usually present in solutions from iron ores, &c.

With a little practice the *rationale* of the method should become clear, and the points at which oxidation and reduction are completed may be determined with accuracy. The experiments should be carefully worked through by the student.

Estimation of Iron in Ore by means of Standard Dichrome Solution.

Before making an assay by titration, the student should practice the exercises set on the previous pages.

Collect the solutions and articles required (see pp. 131 and 132).

Clean the burette, first with water, and then with some of the standard dichrome solution, and fix it on the stand.

Nearly fill the burette with the dichrome solution and adjust to zero.

The ore, having been carefully sampled, and the sample pounded, mixed well, bottled, and labelled, a portion should be withdrawn for assaying. This portion should be finely-pounded in an agate mortar.

Weigh off accurately 1 gramme of the finely-powdered ore.

Transfer it to a 10-oz. conical flask.

Add about 10 c.c. of pure re-distilled hydrochloric acid.

Place a 2-inch funnel in the neck of the flask, and set the whole on a hot plate so as to hasten solution. Solution may be further facilitated by the addition of stannous chloride in re-distilled hydrochloric acid, care being taken to avoid addition of excess.

When all the iron has dissolved, remove the flask, wash the condensed liquid from the funnel and also the contents of the flask into a 7-inch porcelain basin.

Reduce as directed on pp. 135 and 136.

Proceed to titrate as directed on p. 124.

Note the quantity of standard solution taken.

Calculate the percentage.

Example of Calculation.

1 gramme of red hematite ore taken for the estimation.

54·6 c.c. of the standard dichrome solution were

required to complete the oxidation of the iron. Each c.c. of the standard dichrome solution was capable of oxidising 0·01002 gramme of iron.

$$\frac{54{\cdot}6 \times 0{\cdot}01002 \times 100}{1} = 54{\cdot}6 \times 1{\cdot}002.$$

$$54{\cdot}6 \times 1{\cdot}002 = 54{\cdot}71.$$

54·71 = percentage of iron in the sample of ore.

$$54{\cdot}71 \times \frac{10}{7} = 78{\cdot}16.$$

78·16 = percentage of ferric oxide (Fe_2O_3) in the sample.

Estimation of Ferrous and Ferric Oxides in an Ore.

Collect the following solutions and articles on the working bench:—

Standardised dichrome solution (see pp. 131 to 134.

A dilute solution of stannous chloride (see p. 416) in a dropper.

A 5 per cent. solution of mercuric chloride.

A freshly-prepared solution of potassium ferricyanide. This must not be confounded with the more common ferrocyanide. About 0·1 gramme may be dissolved in 100 c.c. of water.

A 2 per cent. solution of ammonium thiocyanate (sulphocyanide).

One or two white porcelain slabs.

Stirring rods for the ferricyanide and the thiocyanate solutions.

A porcelain basin about 7 inches diameter.
A glass rod about 8 inches long.
A reagent bottle containing pure, redistilled hydrochloric acid.
A wash-bottle containing hot water.
A burette stand, and
A burette, graduated in one-tenths.

Select two 175 c.c. (about 6 ozs.) conical flasks. Fit one with a tight-fitting one-hole rubber cork, and the other with a two-hole rubber cork, and to these fit a doubly-bent glass tube, all as shown in Fig. 19.

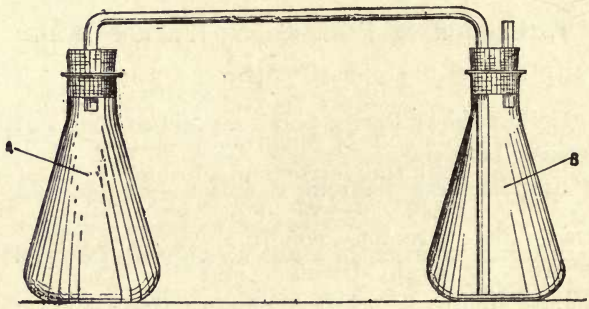

Fig. 19.—Flasks for dissolving iron ore.

Read the general observations on the estimation of iron by means of standard dichrome solution (see p. 131).

For notes on the disintegration of ores, see pp. 251 to 254 of original edition.

Outline of the Process.—On dissolving ore containing ferrous and ferric oxides in hydrochloric

acid, changes take place which may be represented by the equations—

$$FeO + 2HCl = FeCl_2 + H_2O.$$
$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$

Where, as in this instance, it is intended to estimate ferrous and ferric oxides separately, all apparatus and solutions should be in readiness before beginning to dissolve the ore, so that as soon as the ore is dissolved (as far as practicable), titration may be proceeded with before the solution of the ore appreciably suffers from natural oxidation by exposure to air. Precautions are taken to exclude air while the iron in the ore is being dissolved.

The solution from the weighed portion of the ore is titrated with standard dichrome solution. This effects the conversion of the ferrous compound into ferric. The amount of dichrome solution required is noted and all the ferric and chromic compounds are then reduced by stannous chloride to the ferrous and chromous condition. The solution in the basin is again titrated, and the quantity of standard dichrome solution required for this second titration is a measure of the total amount of iron in the ore. The percentage of ferric iron is estimated by difference.

Details of the Process.—Measure about 60 c.c. of boiling distilled water into the conical flask (B, Fig. 19).

Dry the other flask, and put about 1 gramme of sodium carbonate into it.

Weigh off 1 gramme of the finely-powdered sample of the ore.

Transfer the weighed portion to the flask containing the carbonate.

Add 10 c.c. of pure re-distilled hydrochloric acid.

At once close the flask with the cork (which should be moistened) to which the glass tube has been fitted.

Press, with a spiral motion, the cork firmly into the neck of the flask.

Dip the other end of the tube into the hot water in the other flask (see Fig. 17).

Apply heat gently until the iron is dissolved.

Remove the apparatus from the source of heat (hot plate or Bunsen burner), and allow the hot water to suck back into the dissolving flask.

Wash the solution, with hot water, into the basin.

Add about 50 c.c. of hot water.

Run in standard dichrome solution while briskly stirring.

Test from time to time by taking a drop from the basin on the end of the stirring rod and dropping on to a "spot" of potassium ferricyanide solution on the white slab or a piece of drop-reaction paper.

Continue the addition of the standard dichrome solution until, on testing, the desired tint is reached.

The point at which the whole of the ferrous iron has become oxidised to ferric iron is ascertained by placing at intervals a number of drops of a very weak solution of potassium ferricyanide (K_3FeCy_6) on a white glazed tile, and bringing

from time to time, on the point of the glass stirring rod, a drop of the iron solution which is being titrated into contact with one of the ferricyanide drops. As long as ferrous iron remains in the solution a blue precipitate or a blue colouration will result from the mixing of the drops of these solutions. As the indication is developed outside of the bulk of the solution which is being examined, the term "external indicator" is used.

It is essential that this tint should be as near as possible to that at which the operation was stopped when standardising the dichrome.

Read off and note the volume of dichrome solution which has been run in from the burette.

Withdraw the basin, and refill the burette with standard dichrome solution.

Adjust the solution to zero.

Reduce the solution in the basin by adding solution of stannous chloride (see p. 171) while stirring briskly.

Solutions containing ferric iron are reduced by the addition of acid solution of stannous chloride ($SnCl_2$), which is cautiously added, especially as the yellow colour of the ferric solution disappears.

The reaction may be set down thus:—

Fe_2Cl_6	+	$SnCl_2$	=	$SnCl_4$	+	$2FeCl_2$
Ferric chloride	and	stannous chloride	yield	stannic chloride	and	ferrous chloride.

To find the exact point at which the reduction to

ferrous chloride is completed, a drop of the iron solution should be brought into contact with a drop of ammonium thiocyanate (sulphocyanide) solution on a white glazed slab, or on a piece of drop-reaction paper. Where the drops mix with each other a distinct blood-red colour will be shown if ferric iron is present. As the reduction proceeds it will be found that the colour is less distinct as each successive drop is mixed with a fresh drop of the iron solution. When only a faint pink colour results from the joining of the drops, it may be safely assumed that all the ferric iron has been reduced.

When reduction appears to be nearly completed, test for presence of ferric iron.

If necessary, cautiously drop in more of the stannous chloride solution, stir well, and test again.

Continue to add stannous chloride and to test.

When, on applying the test, only a faint pink colour is developed, add about 4 c.c. of a 5 per cent. solution of mercuric chloride to correct, if necessary, any excess of stannous chloride.

Again test on a thiocyanate spot, and make sure that no ferric iron is present.

Run in from the burette two drops of the standard dichrome solution.

Test on a sulphocyanide spot. The contrast between the colour of this last "spot" and the previous one should be quite apparent if all has been properly done.

Complete the titration by the cautious addition of standard dichrome solution.

Note the quantity of standard solution used to complete the oxidation.

Calculate the result.

Example of Calculation.

One gramme of sample of clayband ironstone taken for the estimation.

Each c.c. of the standard dichrome solution was capable of oxidising 0·01001 gramme of iron.

29·93 c.c. of the standard dichrome solution were required to oxidise the ferrous iron, and, after reduction, 31·8 c.c. were required to complete the oxidation of the iron.

Ferrous iron—

$$\frac{29{\cdot}93 \times 0{\cdot}01001 \times 100}{1} = 29{\cdot}93 \times 1{\cdot}001,$$

$$29{\cdot}93 \times 1{\cdot}001 = 29{\cdot}96.$$

29·96 = percentage of ferrous iron.

Total iron—

$$\frac{31{\cdot}8 \times 0{\cdot}0100 \times 100}{1} = 31{\cdot}8 \times 1{\cdot}001,$$

$$31{\cdot}8 \times 1{\cdot}001 = 31{\cdot}83.$$

31·83 = percentage of total iron.

Then, Total iron, . . . = 31·83 per cent
Ferrous iron, . . . = 29·96 „

Ferric iron, by difference, = 1·87 „

Ferrous oxide (FeO)—

$$29{\cdot}96 \times \tfrac{9}{7} = 38{\cdot}52,$$

and 38·52 = percentage of ferrous oxide.

Ferric oxide (Fe_2O_3)—

$$1{\cdot}87 \times \tfrac{10}{7} = 2{\cdot}67,$$

and 2·67 = percentage of ferric oxide.

GENERAL NOTES ON LABORATORY OPERATIONS AND APPLIANCES.

Fine-Pounding or Grinding of Samples.— Friable samples are reduced to very fine powder—"impalpable powder"—in an agate mortar with an agate pestle. To facilitate pulverising, the pestle is mounted in a wooden handle with a ferrule, and the mortar is fitted into a recess in a long piece of hard wood. Very small quantities are ground at a time, and they are reduced to the finest state possible by attrition. The finished sample should be absolutely free from gritty particles.

Weighing is conducted on delicate chemical balances. In institutions where balances are used by junior students it is advisable to always test the accuracy of a balance before using.

The amount of sample weighed off for an estimation depends on the percentage of the constituent to be estimated, the process to be followed, the quantity of the finished precipitate, and on other considerations. A sample of steel for the estimation of carbon by colour requires to be weighed off more accurately than a sample of the same steel for the estimation of sulphur. A sample of rich ferro-manganese for the estimation of manganese requires to be weighed off with greater accuracy than a sample of steel for the estimation of phosphorus. To illustrate this point: Consider what would be the result of an erroneous overweighing to the

extent of 0·001 gramme in each of the above instances:—

2·001 grammes of steel (containing 0·05 per cent. of phosphorus). Result shown, on the assumption that 2·000 grammes had been weighed out for the estimation, 0·050025 per cent.

0·501 gramme of ferro-manganese (containing 80 per cent. of manganese). Result shown, on the assumption that 0·500 gramme had been weighed out for the estimation, 80·16 per cent.

In weighing out small quantities of rich substances it is better to finish weighing with the rider than to attempt to weigh an exact quantity. This is specially the case in weighing out pure materials for standardising.

Finished precipitates require to be weighed very accurately. In estimating sulphur in steel, for instance, an error of 1 milligramme in the final weighing would cause a serious difference in the percentage returned. Such a wide difference is mentioned here to illustrate: it ought never to occur in practice.

Dissolving.—The weighed sample, in the form of drillings or turnings or in powder of the required fineness, may be dissolved in acid or may require to be fused with a suitable chemical. Iron or steel which cannot be dissolved in strong nitric acid may be dissolved in diluted acid if not too weak.

Sulphuric acid of the usual strength (1·84 specific gravity) is, when diluted, used for dissolving substances which are to be titrated with standard potassium permanganate solution.

Fuming hydrochloric acid—water saturated with gaseous hydrochloric acid—contains 42 per cent. of hydrochloric acid. Its specific gravity is 1·21. As usually sold it is diluted to a specific gravity of 1·16, and it then contains 32·02 per cent. of hydrochloric acid. On prolonged boiling of either of these, acid is driven off till a solution containing 20·2 per cent. of acid is reached. A weaker solution loses water on being boiled. For corresponding notes on nitric acid see p. 409, and on sulphuric acid see p. 416. For dissolving in acids under pressure see p. 253.

Fusing.—The sample is intimately mixed with fusion mixture, potassium bisulphate, sodium peroxide, or Stead's reagent, and heated in a nickel, platinum, or silver basin or crucible till the contents become fused or liquefied. Heating is effected in a muffle furnace, or over a blowpipe or a Mecker burner. The latter is very convenient. The "melt," as the liquefied mass is called, is allowed to cool and is afterwards dissolved.

Evaporating excess acid, taking down to dryness and baking or roasting, is carried on in basins or beakers over a hot plate.

The hot plate used by the author consists of 4 cast-iron plates, each 50·5 × 22 cm. (about 20 × 8¾ inches), and each having 7 equidistant rows of 35 studs cast on its under side, each stud being 0·5 cm. ($\frac{3}{16}$ inch) deep and 0·5 cm. diameter, and 1·3 cm. apart from each other. A horizontal gas pipe with small burners or jets is laid under each of the plates. The tips of the flames from the

burners envelop the studs, and the plates are heated with a comparatively small consumption of gas. The heat is sufficient to enable the contents of beakers or basins to be evaporated to complete dryness without changing the residues into that condition in which they cannot be dissolved without difficulty. As the plates are 1·3 cm. (about ½ inch) thick they do not warp or buckle.

Beakers or basins containing liquids which are to be evaporated are placed on a directly-heated plate; wash-bottles may be kept warm, or solutions with precipitates may be set to settle, on the adjoining plates without gas-heating. The four plates are set in a frame, and the arrangement, which was first designed for a Staffordshire steel work, was supplied by Messrs. Fletcher, Russell & Co., Warrington, is very useful in a laboratory.

Evaporating to dryness—in order to bring a washed precipitate into condition for weighing—is generally conducted in platinum or porcelain basins on a water bath. The author uses "platinised nickel" basins—basins pressed into shape from compound sheeting composed of two thin platinum sheets hot-rolled with a central sheet of nickel. These were recommended by the late Prof. Dittmar, and are very convenient for rapidly dealing with phospho-molybdate precipitates. The basins are made with ledges for supporting them over suitable-sized openings in the top of the water bath.

Precipitating, Filtering, and Washing.—These are stages in the separating of one constituent from others.

A precipitate is a solid which is almost, but never absolutely, insoluble in the liquid in which it is precipitated. Precipitation should be effected with the view of forming crystals or granules of definite chemical composition capable of being easily separated from the containing liquid when poured on a filter of porous paper and washed. Generally larger crystals or grains are formed in hot liquids than in cold ones. The larger crystals or granules are not so likely to clog the pores of the filter. A more open or porous filter-paper can, therefore, be used, and washing can be done more quickly. On adding cold ammonium oxalate solution to cold calcium chloride solution, an unsatisfactory precipitate (for washing) is formed. If one of the solutions is hot, a better precipitate appears; if both solutions are at the boiling point a still more satisfactory precipitate is obtained. And if, after the addition of the hot precipitant to the hot calcium chloride solution, the liquid containing the precipitate is boiled, a precipitate is found which settles rapidly, and can be quickly washed with satisfactory results.

In some instances, as in the precipitation of magnesium-ammonium-phosphate, the precipitate should be added drop by drop, and each addition should be accompanied by violent agitation. On the other hand, ammonium molybdate solution should be added all at once.

Some precipitates rapidly subside, and filtration is facilitated if the beaker or flask is set aside in a slanting position so as to cause the precipitate to settle at the bottom towards the side from which the liquid will be poured into the filter. A light, flocculent

precipitate, such as the basic hydrate obtained in the course of the gravimetric estimation of manganese, should be filtered off at once, and quickly washed. The gelatinous precipitate of aluminium hydrate should be quickly washed with hot water, and if, through neglect, it happens to become set, further washing is slow and troublesome.

By saturating the filter with hot water immediately before filtering the operation is considerably facilitated.

Washing aims at the removal from the precipitate of the adhering portion of the liquid in which precipitation was effected and of substances dissolved in it. The washing liquid should be of such a nature as not to dissolve more than the unavoidable minimum of the precipitate. A reasonable quantity of the washing liquid should be used, and allowed to drain off before repeating the washing with another like quantity.

The filter should be smaller than the funnel, and the former should not be more than two-thirds full at any time. The washing liquid, ejected from a wash-bottle, should stir up or plough into the precipitate. The filtrate and washings should not be allowed to splash in the collecting beaker.

The filtrate and washings may in some cases be tested (*a*) to ascertain if sufficient precipitant has been used, and (*b*) to ascertain if the precipitate has been sufficiently washed. If the filtrate is not required (*a*) may be ascertained by collecting some of the filtrate in a test-tube and adding a clear solution of some of the substance to be precipitated. Presence of a precipitate in the test-tube is sufficient evidence. To apply test

for (*b*) some of the latter washings may be allowed to drop into a test-tube and a clear solution containing a substance which can cause a precipitate added. Thus, to test if a magnesium-ammonium-phosphate precipitate has been washed enough, a clear acidified solution of silver nitrate is added to some of the last washings collected in a test-tube. If the collected washings contained chlorides a white precipitate of silver chloride will form. Absence of a precipitate is good evidence of thorough washing, but, to be quite safe, it is advisable to wash two or three times more.

When the filtrate is required for further analysis, no portion can be permitted to be withdrawn for testing. But if the power of the measured quantity of precipitating solution is known, and is compared with the weight of the precipitate, a safe inference may be drawn.

When precipitation is properly carried on—with due regard to conditions—filtering and washing may, in most instances, be quickly and efficiently effected in ordinary filters of good filter-paper. Many contrivances are in use for facilitating filtering—such as filter pumps, bell jars and suction pumps, Gooch crucibles (crucibles with bottoms having numerous small perforations) for working with pumps, and asbestos or pulp filters.

Asbestos filters are prepared by igniting fine-fibred asbestos, allowing to cool, placing in a clean mortar along with water, rubbing with a pestle till the fibres are bruised and broken, pouring the pulp produced

into a Gooch crucible, draining till dry (the filter pump being used), and repeating the washing and draining till no more fibres are washed through. For some purposes asbestos washed with acid may be used instead.

Regarding **pulp filters**, the following notes contributed by Ibbotson to "Technics" give full practical details for preparing and using them as recommended by Horace Jervis (*Chemical News*, 78, p. 257):—

"Ashless filter-paper clippings are torn into small pieces and vigorously shaken in a bottle with considerably more distilled water than they can absorb. In less than five minutes a filtering medium of fine texture is thus obtained. A porcelain filter plate, $\frac{7}{8}$ inch in diameter, and pierced with about twenty holes each nearly $\frac{1}{16}$ inch in diameter, is placed in the throat of a *smooth* funnel of $3\frac{1}{4}$ inches diameter. Closing the stem of the funnel with the thumb of the left hand, water is then poured on in sufficient quantity to fill the stem and cover the plate, care being taken that no air is imprisoned below the latter. Sufficient pulp is then poured on to give a thickness of felting, for ordinary purposes, of no more than a $\frac{1}{4}$ inch; and having adjusted the plate in a horizontal position by means of a glass rod, the thumb is removed and the water allowed to run away, whilst a rotary motion is imparted to the funnel. By means of a spatula or pair of weight pincers, the felting is then pressed slightly and the edge tucked in, so as to prevent a rise of the pulp when liquids are poured on.

"The funnel may then be arranged for suction;

sufficient pressure may easily be induced by the mouth without resorting to the use of a filter pump.

"A precipitate is effectively and rapidly washed by filling up the funnel twice, and after sucking the water from the stem of the funnel, which is full of liquid throughout the filtration, it only remains to transfer the precipitate (which has been rendered sufficiently dry by the suction) to the ignition dish or crucible. This operation does not at first commend itself to the manipulator. By means of a pair of weight-pincers the edge of the pulp is lifted at any point, and the felting folded over about a horizontal diameter, so as to bring the under surface uppermost. This surface is then grasped by the pincers and the whole filter bodily transferred, precipitate side underneath, to the ignition dish, in which a dry piece of ashless paper has been previously placed. The precipitate, which is still moist, does not therefore make actual contact with the platinum. It now only remains to transfer the small amount of precipitate clinging to the sides of the funnel above the region previously occupied by the pulp. The funnel is grasped in the left hand, leaving the thumb free to rotate it by pressure applied at the rim, whilst a small piece of wetted ashless filter-paper is tightly pressed (by means of the thumb only of the right hand) against the side of the funnel. By gradually bringing the paper from throat to rim during the rotation it will be found possible in most cases, after a little practice, to remove every trace of adhering precipitate by means of a small piece of paper.

"The total amount of paper to be burnt off in the

event of its being found necessary to use a second piece for cleaning the funnel is considerably less than the reader might think; and no harm can be done by making absolutely certain of the thorough cleansing of the funnel by the use of still more paper.

"Precipitates of the barium sulphate type are effectually retained by using a thicker layer of pulp, but no advantage over ordinary filter-papers can be claimed for pulp when handling gelatinous precipitates of the zinc sulphide type.

"**Ignition** may be commenced at once, or at any rate, after rapidly drying at the mouth of the muffle; and when completed, the ignited residue may be entirely brushed from the crucible, of which the weight is therefore not required.

"All precipitates which may be safely ignited in contact with the paper—and their number is considerably greater than a perusal of text-books on quantitative analysis would lead one to suppose—may be treated as described. The extinction of the last spark, which generally takes place in the centre of the mass, is a guarantee of complete and thorough ignition."

Ignition of filter-paper in contact with certain precipitates, such as ammonium-magnesium-phosphate, is at times troublesome unless precautions are taken.

The ignition should be cautiously begun, so as to avoid highly heating the precipitate before the organic part of the filter is burnt away. The precipitate should be white (not grey) before removing the capsule to the hottest part of the muffle, where it should

remain for an hour. Unless this is done, there is danger of the precipitate so clinging to the filter-paper that it becomes difficult to burn off the paper.

When **decomposition** has to be effected—as in the conversion of calcium oxalate into calcium oxide, or the conversion of the hydrated manganese peroxide precipitate to tri-manganic tetroxide—prolonged ignition in a muffle furnace at a high temperature is required. By using a Mecker burner with blast, these changes may be completed in a few minutes. Ignited precipitates must be allowed to cool down in desiccators, otherwise they would absorb moisture from the atmosphere.

Comparing Colour-depths.—In American works the colorimetric estimation of carbon in furnace samples and finished steel is facilitated by various contrivances. The test piece is rolled through a set of small rolls, or is hammered to form a bar about 8 inches × 1 inch × ½ inch, stamped, and allowed to cool on a firebrick slab. It is then placed in a special machine with a horizontal drill. When the skin has been cleared, drillings fall through a funnel into a removable scooped pan which is set on the beam of a delicate balance. The weighing having been quickly completed, and the weighed drillings transferred to a test tube, the measured quantity of nitric acid is dropped in. The test tube is then placed in a bath containing an aqueous solution of calcium chloride, which is kept at its boiling point (110° C.) by high-pressure steam. When the sample is completely dissolved, the test tube is set in a cold-water

vat to cool. The liquid is then transferred to a graduated Eggertz' comparison tube of about 30 c.c. capacity, the upper part of which is bent to an angle of about 115°, and terminates in a small enlargement or funnel. This style of comparison tube facilitates pouring, and the mixing of the contents by shaking.

In comparing depth of colour, the standard Eggertz' tube and the comparison tube are placed in a box or "camera" in a dark room. The camera is blackened within on four sides. Light from an incandescent burner is admitted through a ground-glass plate screened by blue tissue paper. The ground glass disperses the light, and the blue-coloured paper neutralises the yellow rays of light.

For comparing coloured solutions there are several forms of **chromometers**. One of the best known in steel works is that devised by Mr. J. E. Stead for use in estimating carbon in steel, and described by him in the *Iron and Steel Journal*, 1883, vol. i., p. 217. It consists of two parallel measuring tubes of similar diameter, each about 23 cm. (9 inches) long. These are mounted on a suitable frame having graduation marks and carrying a white disc near the bottom and a reflector at the top. A connection can be made between one of the tubes and a wide-neck bottle—generally of about 120 c.c. capacity—for the solution of standard steel. A syringe is also connected (see Fig. 9).

In working with the chromometer a quantity of the solution from the steel to be tested is placed in the left-hand measuring tube. On squeezing the

syringe, the standard solution is forced into the other measuring tube to form a column which will show a corresponding depth of colour. The percentage is then calculated (see p. 10).

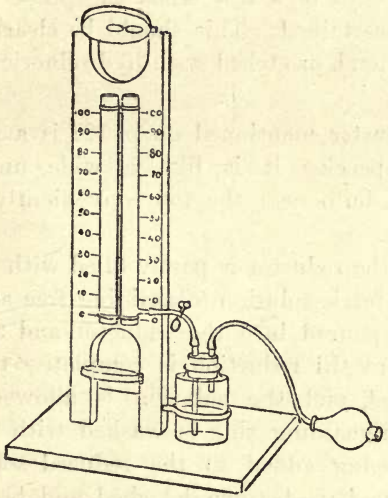

Fig. 9.—Stead's Chromometer.

For volumetric estimations standard solutions and indicators, which readily show a definite "end point," are required. These are fully dealt with in the preceding pages.

For volumetric work, accurately graduated burettes, flasks, &c., may be purchased at very reasonable prices. Pipettes for the estimation of phosphorus in pig iron may be standardised by finding the specific gravity of the solution of pig iron—by means of a 50 c.c. specific gravity bottle—and then finding (by weighing into a

tared beaker) the level in the pipette from which 20·38 c.c. of the solution are delivered. A slip of gummed paper is fastened on the stem, and levels are tentatively marked thereon with pen or pencil. From the result of a few trials the proper level can be easily ascertained. This should be clearly marked with a diamond, or etched with hydrofluoric acid.

The **reductor** mentioned on p. 127 is a glass tube with a stopcock : it is like a wide ungraduated burette. A bulb near the top conveniently increases its capacity.

For use, the reductor is partly filled with pure zinc shot. The ferric solution (containing free acid) to be reduced is poured into the reductor and allowed to remain there till reduction is complete; the tap is then opened, and the solution is allowed to flow out. The remaining zinc is washed with water, the washings being added to the reduced solution. If pieces of zinc have become detached and been carried down with the solution, a little mercuric sulphate (see p. 128) should be added to coat the zinc and prevent further action. Titration may then be proceeded with.

NOTES ON PREPARING AND STORING SOLUTIONS.

Solutions for analytical purposes should be prepared from pure chemicals, and stored in well-stoppered stock bottles (half-Winchesters suit well for many of the solutions) in a store-room screened from direct sunlight and situated in a convenient part of the laboratory.

The shelves should be arranged at suitable distances from each other, and the place for each bottle should be marked by a clearly-printed label carefully covered with paraffin wax. Each stock bottle should have a clearly-printed, wax-covered label. The labels of each row should be arranged on the same level—those for the top row being placed near the bottom of the bottles, those for the bottom row near the top, and those for the intermediate rows placed in intermediate positions, each row differing from the others. Bottles which are thus symmetrically labelled are easily kept in their respective places. If, by mistake, a bottle is placed on a wrong shelf, the error is at once detected, and its proper place is soon found.

Many of the solutions may be conveniently made up in stoneware jugs. These are not so tender as glass ware

Acetic Acid cooled below 15·5° C. forms large, colourless, transparent crystals. Above that temperature these melt and yield a colourless, pungent liquid known as **glacial acetic acid,** which has a density of 1·063. As usually sold, its specific gravity is 1·045, but the strength of this acid cannot with certainty be ascertained by its density. The weight of dry sodium carbonate required to neutralise a measured quantity is a safer guide.

Ammonia liquor, or **liquor ammoniæ,** is a solution of gaseous ammonia in water. The higher the percentage of ammonia in solution the lower its specific gravity. As usually sold it has a specific gravity of 0·88 at 15° C. This saturated solution contains 35 per cent. of ammonia.

Ammonium Acetate.—Neutralise 1·045 specific gravity acetic acid exactly with 0·88 specific gravity ammonia liquor, using phenolphthalein or litmus as indicator.

Ammonium Chloride.—Dissolve 200 grammes of pure ammonium chloride in hot water, and make up with cold water to 1 litre.

Ammonium Molybdate.—Weigh off 50 grammes of pure molybdic acid, stir into 100 c.c. of water, and dissolve in 100 c.c. of 0·88 specific gravity ammonia liquor. Pour the solution into 750 c.c. of *cold* 1·20 specific gravity nitric acid (see p. 168). Stir

vigorously, or, by means of a foot-bellows, blow air through the dilute nitric acid while adding the other solution. Allow to settle, and, if necessary, filter through a double close-texture filter into the stock bottle.

J. E. Stead uses (see p. 32) a 10 per cent. solution of ammonium molybdate in water. This is used in conjunction with excess of nitric acid.

Ammonium Nitrate.—Dissolve 2 lbs. of pure ammonium nitrate in warm water, filter the solution if necessary, make up with cold water to 1·5 litres, and mix well.

One kilogramme may be similarly treated and made up to 1,650 c.c.

Ammonium Oxalate.—Dissolve 100 grammes of pure ammonium oxalate in $2\frac{1}{2}$ litres of hot water.

Or, dissolve $\frac{1}{4}$ lb. (113 grammes) in $2\frac{3}{4}$ litres of hot water. When cool, make up with water to 2,825 c.c. and mix well.

One c.c. of this solution can cause the precipitation of calcium oxalate equal to 0·0177 gramme of lime.

Ammonium Persulphate.—In order to get a sharp reaction on the addition of this reagent, it is necessary that it should be slightly moistened a few hours before being used. If moistened a day or two beforehand, a sharp reaction may be had. Persulphate may be used instead of bromine in the gravimetric estimation of manganese.

Ammonium Phosphate.—Dissolve 200 grammes of pure ammonium phosphate in 1 litre of warm water. When cool, make up to the 1,000 c.c. mark with cold water and mix well. Or, dissolve ½ lb. (226 grammes) and, when cold, make up with water to 1,130 c.c. and mix well. This solution does not keep well.

One c.c. of this solution can cause the precipitation of ammonium-magnesium-phosphate equal to 0·023 gramme of magnesia.

Ammonium Thiocyanate (Sulphocyanide) for Indicator.—Dissolve 2 grammes of the pure salt in 100 c.c. of water. This solution does not keep well.

Aqua Regia.—Mix 3 volumes of 1·16 specific gravity hydrochloric acid with 1 volume of 1·42 specific gravity nitric acid for use when required.

Barium Chloride.—Dissolve 100 grammes of pure barium chloride in about 300 c.c. of warm water. When cool, make up to 1,000 c.c with cold water and mix well. 10 c.c. of this solution can cause the formation of a precipitate of $BaSO_4$ weighing 0·955 gramme.

Cadmium Acetate.—Dissolve 25 grammes of pure cadmium acetate in 500 c.c. of water, add 100 c.c. of glacial acetic acid, and make up with water to 1 litre.

Cadmium Chloride.—Dissolve 40 grammes of pure cadmium chloride in 1 litre of water, add 1 litre of 0·88 specific gravity ammonia liquor and mix well.

Caustic Potash.—See Potassium Hydroxide, p. 169.

Caustic Soda.—See Sodium Hydroxide, p. 170.

Hydrochloric Acid is a colourless gas with a very pungent smell. It is extremely soluble in water. At ordinary temperature and pressure a solution containing 42·9 per cent. of the acid may be obtained. The specific gravity of the saturated solution is 1·212. As usually sold "hydrochloric acid" has a specific gravity of 1·16. When of this density it contains 32·02 per cent. of HCl. Weak aqueous solution of hydrochloric acid loses water when boiled and becomes stronger; a strong solution when boiled loses gas and becomes weaker. In both cases the result is an acid containing 20·24 per cent. of HCl.

Pure hydrochloric acid should be used for analysis.

Hydrochloric Acid of 1·1 Specific Gravity.—To 250 c.c. of 1·16 specific gravity hydrochloric acid add 150 c.c. of water and mix well.

Hydrofluoric Acid.—The aqueous solution of hydrofluoric acid is a corrosive irritating liquid which readily attacks glass vessels. It is, therefore, kept in gutta-percha bottles, which should be kept carefully closed with gutta-percha stoppers. It is seldom sold in a state of purity, and when a few drops are evaporated in a platinum dish (in a fume cupboard, of course) a solid residue is left. The weight should be ascertained and allowed for as a "blank."

Hydrogen Peroxide.—This may be purchased of the required strength, or may be prepared by triturating barium peroxide with water and adding hydrochloric acid and more water. It may also be prepared by acting on sodium peroxide with nitric acid and water.

Iodine Solution for Sulphur Estimation.—Weigh off 2 grammes of re-sublimed iodine and dissolve in 50 c.c. of water containing 4 grammes of potassium iodide. When the iodine has dissolved, make up with water to 1 litre and mix well. Standardise, as directed on pp. 48-51, before using, or if in regular use, re-standardise every third day. If used occasionally, re-standardise before using. Iodine solution should be kept from light in a cool cupboard.

Iron Solution for "Correction" in Gravimetric Estimation of Manganese (p. 38).—Dissolve 0·0177 gramme of fine iron wire (pianoforte wire) in hydrochloric acid, and make up with water to 1 litre.

Magnesia Mixture.—Dissolve 25 grammes of pure magnesium chloride ($MgCl_2,6H_2O$) and 25 grammes of pure ammonium chloride in 400 c.c. of water. Add 200 c.c. of 0·88 specific gravity ammonia liquor and mix well It is advisable to prepare this solution some time beforehand, and to decant the clear liquid or separate any precipitate which forms by filtration.

One c.c. of this solution may be assumed to be capable of causing the formation of a precipitate of ammonium - magnesium - phosphate containing 0·01 gramme of phosphorus.

Mercuric Chloride.—Dissolve 25 grammes of mercuric chloride in 500 c.c. of warm water.

Methyl Orange for Indicator.—This solution may conveniently be purchased.

Nitric Acid is a colourless, fuming, corrosive liquid, having a specific gravity of 1·53. As usually sold it is diluted with water till its specific gravity is about 1·42. At 1·42 the solution contains 69·34 per cent. of nitric acid.

When strong nitric acid is boiled it is partially

decomposed, nitrogen peroxide and water being formed. When weak nitric acid is boiled, water is driven off. Thus, whether strong or weak, the acid, on being boiled loses either nitric acid or water until the strength reaches 68 per cent. of NHO_3.

For analytical work pure acid should be used.

Nitric Acid, Dilute, for Carbon Estimation.—Add 200 to 210 c.c. of 1·42 specific gravity nitric acid to 250 c.c. of water and mix well. The specific gravity of the liquid should be about 1·20 when cool. Test with the hydrometer. If required, add either acid or water to correct the density.

Nitric Acid, Dilute, for Volumetric Estimation of Phosphorus.—To 2,500 c.c. of water add 25 c.c. of 1·42 specific gravity nitric acid, and mix thoroughly. The strength of this dilute solution may be ascertained by titrating with standard solution of sodium carbonate. It should also be standardised with the sodium hydroxide solution which is to be used in the phosphorus estimation.

Phenolphthalein for Indicator. — Dissolve 1 gramme of the powder in 300 c.c. of alcohol and add 250 c.c. of water. Add clear, dilute solution of sodium or potassium hydroxide, drop by drop, till the solution becomes pink coloured ; then add dilute nitric acid solution till the colour is just discharged. A prepared solution may conveniently be purchased.

Potassium Dichromate (Dichrome) — Standard Solution for Volumetric Estimation of Iron.—This is prepared and standardised as directed on pp. 131 to 134.

Potassium Ferricyanide for Indicator.—Dissolve about 0·10 or 0·20 gramme of pure potassium ferricyanide in about 100 c.c. of water. Only freshly-prepared ferricyanide solution should be used.

Potassium Hydrate.—See below.

Potassium Hydroxide (Potassium Hydrate or Caustic Potash) for Combustion.—Dissolve 105 grammes of pure potassium hydroxide in water and make up to 250 c.c. with more water. Keep in a bottle with a tight-fitting cork.

Potassium Permanganate—Standard Solution for Volumetric Estimation of Iron.—Prepare and standardise as directed on pp. 121 to 125

Potassium Permanganate for Volumetric Estimation of Phosphorus.—Dissolve 4·264 grammes of potassium permanganate in water, and make up with more water to 1 litre.

Silver Nitrate for Colorometric Estimation of Manganese in Pig Iron.—Dissolve 4 grammes of pure silver nitrate in water, make up to 1 litre with water, and mix well. If, on standing, a precipitate settles out, treat as above. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Colorometric Estimation of Manganese in Steel.—Dissolve 1·33 grammes of pure silver nitrate in water, make up to 1,000 c.c. with water, and mix well. Allow to settle, and, if necessary, filter. If, in consequence of the water not being quite pure, there is more than a slight precipitate, more silver nitrate should be added, and the clear solution filtered off. Keep in an amber-coloured bottle or in a dark place.

Silver Nitrate for Testing Washings.—Dissolve 2 grammes of silver nitrate in 500 c.c. of water, add 500 c.c. of 1·42 specific gravity nitric acid. Allow to stand for a little, and, if necessary, filter. Keep in an amber-coloured bottle or in a dark place.

Sodium Hydrate.—See Sodium Hydroxide below.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Sulphur Estimation.—Dissolve 56 grammes (or 2 ozs.) of pure sodium hydrate in 1 litre of water. Allow to stand for some hours, and, if any sediment has formed, separate the clear portion of the solution by decantation.

Sodium Hydroxide (Sodium Hydrate or Caustic Soda) for Volumetric Estimation of Phosphorus.—(*a*) Stock solution. Dissolve 68 grammes in water, and, when cold, make up with water to 1,000 c.c. (*b*) Working solution. Draw off 250 c.c. of the stock solution, make up with water to $2\frac{1}{2}$ litres, and mix thoroughly.

Stannous Chloride (Strong).—To 15 c.c. of water add 30 grammes of pure stannous chloride and stir for a few minutes. Add 450 c.c. of 1·16 specific gravity hydrochloric acid, and heat gently to about 70° C. Continue the stirring to dissolve as much as possible of the salt. If an insoluble residue remains, allow it to settle. Pour off the clear liquid into a suitable bottle. Store in a cool, dark cupboard. On long standing a precipitate of stannic chloride sometimes forms.

Stannous Chloride (Dilute).—Measure off 10 c.c. of the strong stannous chloride solution, make up to 100 c.c. with water, and charge into the dropper for finishing reduction of ferric solutions.

Starch Solution.—Make 1 gramme of potato starch into a thick cream with a little cold water by stirring in an 18 cm. (about 7 inches) diameter porcelain basin. Quickly pour into the cream 500 c.c. of boiling water while stirring vigorously. Boil the solution for two or three minutes, and allow it to cool before using. A starch solution prepared in this manner may remain in good condition for a few days.

Sulphuric Acid is a heavy, oily, colourless liquid, which when strong and pure has a specific gravity of 1·854. When boiled it is decomposed, and gives off sulphur trioxide, as indicated by the equation, $H_2SO_4 = SO_3 + H_2O$, until 1·5 per cent. of water is present, after which it distils unchanged.

As usually sold, its specific gravity is 1·84. This strong acid should be cautiously diluted by pouring into water.

Sulphuric acid sold as "pure" sometimes contains lead in solution, which separates on dilution.

Sulphuric Acid, Dilute No. 2 (sp. gr. 1·26), for Dissolving Steel.—Cautiously pour 250 c.c. of 1·84 specific gravity sulphuric acid into 750 c.c. of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphuric Acid, Dilute No. 4, for Use in Sulphur Estimations.—Cautiously pour 100 c.c. of 1·84 specific gravity sulphuric acid to 1 litre of water. Allow to settle for some days. Pour off from any settled precipitate into a bottle with a well-ground glass stopper.

Sulphurous Anhydride or Sulphurous Acid.—Syphons containing water highly charged with this gas may be purchased. When the charged syphon

is in an upright position, gaseous anhydride will be delivered on opening the tap. But when the charged syphon is laid horizontally, the anhydride in aqueous solution will be delivered on opening the tap. 5 or 10 per cent. aqueous solutions may also be purchased.

Zinc Chloride.—Dissolve 100 grammes of pure zinc chloride in 1 litre of water.

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